FINAL REPORT

ELECTRONIC NOSE: NEW TECHNOLOGY INFUSION

Advanced Environmental Monitoring and Control for Space Station

April 30, 1999

M. A. Ryan
Mail Stop 303-308
Jet Propulsion Laboratory

(818) 354-8028
mryan@jpl.nasa.gov

JET PROPULSION LABORATORY
California Institute of Technology
Pasadena CA 91109

1. INTRODUCTION

This is the final report for the program "Electronic Nose: New Technology Infusion" funded under Advanced Environmental Monitoring and Control for Space Station, NASA Code UL. This program extended the proof of concept work done on polymer-based sensors for an Electronic Nose, done by Prof. N. S. Lewis at California Institute of Technology. Prof. Lewis' work identified and demonstrated the operation of polymer based sensors for use in sensing arrays [1-3]. The program at JPL built on Prof. Lewis' work to build a prototypical miniature Electronic Nose. That ENose was flown on STS-95 in an experiment to determine its utility as an air quality/incident monitor in crew habitat on a spacecraft. This program was successful in building a prototypical model, designing data acquisition and control, designing data analysis software, and in monitoring crew quarters air for a group of compounds in concentrations greater than the 1 hour Spacecraft Maximum Allowed Concentration (SMAC). The list of compounds and their SMACs are found in Table 3.1.

The rationale behind this program is that there are, at present, no miniature gas sensors which are capable of detecting and identifying a broad suite of compounds. Analytical instruments such as a gas chromatograph-mass spectrometer are capable of highly accurate analysis at very low levels, but require significant crew time to operate and maintain. Contaminants in the breathing air in an enclosed space such as the crew quarters of the space shuttle or space station are difficult to detect because of the lack of such a monitor; however, the need for such a capability is clear. As the air in the space station cannot be easily replaced, and because there are contaminants which are likely to build up over time, it is important for crew health that air quality be monitored at levels ranging from the 7 day SMACs to greater than the 1 hour SMAC.

Transient contaminants may build up in the filtering systems, and compounds which cannot be as easily removed by filtering will remain in the breathing air and are cause for concern. In addition, toxic contaminants may be released as a result of episodic events such as fires or spills, as well as by outgassing. Present plans for air quality monitoring on the space station include an ion mobility spectrometer and electrochemical sensors for specific combustion products. Such devices are limited by power and weight restrictions as well as by the number of compounds detectable. In addition, extensive crew time is required to operate such monitors. The need, then, is for low power gas monitors which can be operated with a minimum of crew time and which can be networked into space station operating protocols.

The ultimate goal of this new technology infusion is to create an integrated environmental monitoring and control system for the International Space Station and beyond. Reaching this goal will involve the rapid, early insertion of advanced, novel technologies in three steps. This program addressed Step One, which is the development of an Autonomous Electronic Nose and flying it as an experiment on a shuttle mission. The purpose of this step is the demonstration that the technology can be developed to be used as an air-quality or incident monitor in crew habitat. Step Two involves further miniaturizing the device so that a network of autonomous electronic

noses can be integrated on the Space Station. In such a network, multiple sensors will function separately while a central system collects and analyzes data. Step Three involves the integration of environmental control with the monitoring functions developed in steps one and two.

There are several sensors which are specific to particular compounds or classes of compounds, but using compound-specific sensors to monitor changes in breathing air is a task which would involve the use of several hundreds of sensors. In addition, compound-specific sensors are subject to interference from molecules of structure similar to the target molecule. Analytical instruments such as gas chromatography-mass spectrometry (GC-MS) have multi-compound capability, but are impractical for continuous monitoring. Work on the electronic nose was designed to fill the gap between individual, chemically specific devices and analytical instruments such as GC-MS which have multi-compound capability.

Multi-compound sensing may be accomplished using an array of partially specific sensors, or an electronic nose. In an electronic nose, the distributed response of an array of several sensor heads is used to identify the changes in the composition of a gaseous environment. This is accomplished by comparing the response of the array to a baseline response of known, "good" air. Sensors are not specific to any one gas; it is in the use of an array of sensors with a different sensing medium on each that gases and gas mixtures can be identified by the pattern of response of the array. To date, sensor arrays have been used only in fairly restricted applications, such as the controlled atmosphere of quality control for beer or coffee manufacture. There are commercially available electronic noses, which are neither miniature nor low power.

A commonly used sensing medium in other electronic noses is SnO_2 or other metal oxide thin films, which present some difficulties in reversibility and reproducibility as well as high power consumption. Conductive polymer sensing media have also been studied and have been used with some success, the films tend to have short lifetimes [4,5]. In this program, the sensor heads are conductometric sensors which use a thin film of insulating polymer loaded with a conductive medium such as finely divided carbon as the sensing layer, and operate at or near room temperature. When new compounds are present in the previously established baseline, the resistance of the conducting polymer film changes, and the pattern of response of the sensors makes it possible to identify the compound or compounds and concentrations responsible for the change in response.

JPL has developed, built and demonstrated a low power, miniature gas sensor which has the capability to distinguish among and identify various gas species which may be present in the recirculated breathing air of the space shuttle or space station. This effort included development and optimization of sensing films, development of electronic interfaces between sensors and a portable computer, and development of data analysis software to identify and quantify selected contaminants singly or in a mixture of contaminants. The JPL ENose device which was demonstrated on STS-95 weighs 1.4

kg including the computer for control, has a volume of 1700 cm^3 (18.5 cm x 11.5 cm x 8 cm), and uses an average power 1.5 W (3 W peak power).

2. OBJECTIVE

The objective of this work was to develop, build and demonstrate a miniature gas sensor, an Electronic Nose, for experiment on a shuttle flight. The prototypical sensor was to be capable of monitoring the cabin environment for the presence of 12 contaminants at the one-hour Spacecraft Minimum Allowable Concentration (SMAC) levels or below. The target compounds were:

methanol	ammonia	formaldehyde	indole
ethanol	benzene	Freon 113	methane
2-propanol	CO_2	hydrazine	toluene

In addition to these compounds, the ENose was built to be capable of detecting changes in humidity.

Two compounds were eliminated from the list after the program began. Carbon dioxide was eliminated because the polymer sensors used were insufficiently sensitive to that compound. Hydrazine was eliminated because of safety concerns in handling that compound in the ENose lab at JPL. One target compound was added to the list; that compound is the 2-propanol wipe which was used to verify device operation during the flight. The exact composition of the wipe is not known.

The ENose fabricated was a complete device, consisting of 32 sensors in an array, electronics to allow control of the array as well as to read the response and transfer data from the array to a computer, and a computer for instrument control and data acquisition and storage. Design of data analysis and software to allow identification and quantification of the target compounds list was included in the program. Although the original intention of the program was to develop real-time data analysis, after consultation with the co-investigator, Dr. John James of the Toxicology Branch at Johnson Space Center, it was determined that post-flight analysis would be preferable to running the risk of false positive data analysis in real time. Analysis was done after the flight.

In pursuit of the objective, the work to be done was divided into development tasks and integration tasks. The development tasks included work on sensors, electronics, and analysis software. There were two integration tasks in this program: coordination of the flight experiment with JSC, and integration of the three development tasks in order to design and fabricate the flight unit.

Success criteria were set for the overall program in consultation with the co-investigator at JSC, with the condition that the ENose experiment would not take place in flight

unless 80% of the success criteria for ground testing had been met before the flight. Sufficient criteria were met before flight, and the experiment went as planned. The success criteria for ground test and for flight are listed below, and are discussed in the various relevant sections of the report and the criteria and how they were met are summarized in Section 9.

2.1 Success Criteria For Ground Testing

1. Target compounds can be detected, identified and quantified at +/- 50% the one-hour SMAC level or lower by applying the analysis software developed for the purpose.
2. Mixtures of 2 & 3 targeted gases can be detected, identified and quantified at +/- 50% the one-hour SMAC level or lower by applying the analysis software.
3. Contaminants in a pre-mixed sample of 4 gases, can be identified and quantified at +/- 50% the one-hour SMAC level or lower by applying the analysis software.
4. ENose data analysis segregates compounds which are not on the target list.

2.2 Success Criteria For Shuttle Flight Experiment

1. Successful delivery and acceptance to flight.
2. Device operates continuously (while turned on) as programmed, and data are retrieved after flight.
3. Sensor responses correlate with the shuttle logged events of sufficient concentration.
4. Data analysis software correctly identifies and quantifies planned events.
5. Data analysis software correctly identifies targeted compounds at or above the one-hour SMAC level and quantifies them at +/-50%, confirmed by the GC-MS analysis of the Grab Sample Container contents.
6. Data analysis software classifies as "unknown" compounds which are detected and are not on the target list.

3. SENSOR DEVELOPMENT

3.1 Sensing Films

Successful development of an electronic nose requires development of an array of sensors which are partially specific to the compounds of interest. The sensing media in the ENose developed in this effort were insulating polymer films made conductive by dispersion of carbon particles in the film. These sensing films respond to a change in air composition with a change in resistance. The resistance change in the array is characteristic of the compound causing it. For this phase of ENose development, only the magnitude and pattern of response were considered in film selection, as the kinetics

of sensor response were obscured by the time for target compounds to be delivered to the sensors by the gas delivery system.

Several steps are included in the development of the film. These steps include selection of polymers, selection of sensor geometry, design of sensor head, fabrication of sensor chips, development of a laboratory data acquisition system, and characterization and testing of sensing films and sensor head.

Before the start of this program, the research group of Prof. Nathan S. Lewis at Caltech had done extensive work in identifying polymers from which to make films for application in the electronic nose. Prof. Lewis and his group were involved in this stage of the development effort by providing the data necessary to select the polymer films to be used. Prof. Lewis' group provided JPL with response data for 85 polymers mixed with carbon particles. From those data, statistical analysis determined the polymer films with the greatest difference in magnitude and pattern of response for each target compound. A set of 25 polymers was generated from this analysis. Tests of solubility of the polymers in organic solvents and of the ability of the polymer solution to disperse carbon and produce a homogeneous film were used to further narrow the list to 16 polymers. The polymers selected for use in the flight unit of the ENose are listed below. The order in which they are listed corresponds to the order in which the data for that polymer are reported in the response files.

C71	Poly(2, 4, 6-tribromostyrene), 66%
A	poly(4-vinylphenol)
Q	poly(ethylene oxide)
C38	Polyamide resin
C7	Cellulose triacetate
C58	Poly(2-hydroxyethyl methacrylate)
C90	Vinyl alcohol/ vinyl butyral copolymer, 80% vinyl butyral
E15	Poly(caprolactone)
E3	Poly(vinylchloride-co-vinyl acetate)
E4	Poly(vinyl chloride-co-vinyl acetate) 10%vinyl acetate
E6	Poly(vinyl acetate)
E5	Poly(N -vinylpyrrolidone)
C88	Styrene/isoprene, 14/86 ABA Block copolymer
C80	Poly(vinyl stearate)
C22	Methyl vinyl ether/ maleic acid 50/50 copolymer
C20	Hydroxypropyl methyl cellulose, 10/30

The polymers used in this program were selected from the set tested by Prof. Lewis' lab, but the pool of polymers was not optimized for response to the target compounds. Further development of the ENose will focus on determining an approach to selection of the set of polymers for a set of target compounds which is based in the theory of chemical interaction of the analytes and the sensing films (see Section 10).

In addition to selection of the polymers with which to make the sensing films, it was necessary to select the geometry of the electrode pairs across which resistance is measured. Before the start of this program, work at JPL had developed a test chip to be used for determination of the geometry of the sensor. The test chip was made by screen printing thirteen sets of gold-palladium electrodes on a co-fired ceramic substrate; polymer films were then deposited on each set of electrodes in order to make a chip with several sensors. The prior work at JPL had also developed a concept for the data acquisition hardware and a bread-board for data acquisition had been made.

Using the data acquisition hardware and software already developed at JPL, several test chips were tested. Films were deposited on the sensors on the test chip, and response to infusions of target compounds in air were studied. Response magnitude, reproducibility and noise level were considered in order to select the best sensor geometry.

The design of the test chip is shown in Figure 3.1. The chip is 25 mm X 10 mm. The various geometries were tested for magnitude of response and noise level to determine which was the best for the ENose. In the course of these experiments, it was determined that the U-bend shape (sensors S4-S7) gave the most reproducible, lowest noise response. Sensor S6 was chosen for the flight design.
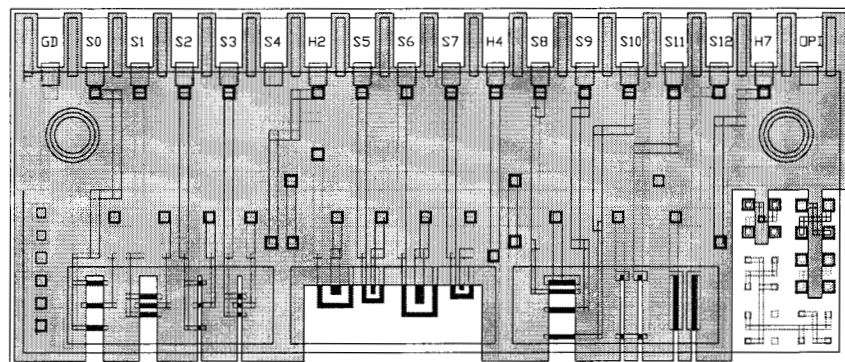
Figure 3.1. Design of the co-fired ceramic test chip with 13 Au-Pd electrode pairs. Polymer films were deposited on the electrode pairs and resistance measured across the film.

3.2 Laboratory Testing

Sensing films developed were tested in the laboratory to determine the characteristics of the film response to contaminant. These characteristics include noise level, the limit of response, recovery time, the pattern of response across the polymer film array, and the linearity of response with concentration. Film development required several

iterations of deposit and test to determine the best conditions for making the film. It was determined that a film with a baseline resistance (in clean air) of 5-50 kΩ gave a response with the best signal to noise ratio and the fastest recovery time. All films were deposited with resistance in this range. Thickness was not controlled; each polymer film had a different thickness for it to fall within the desired resistance range.

In this phase of the program, it was found that the baseline resistance in many of the polymer films is significantly affected by changes in temperature of as little as 0.1°C. This change in baseline is seen in the data as baseline drift. In order to minimize the data analysis task, RuO_2 heaters were included in the manufacturing process on the back of each ceramic chip to provide a constant temperature on the sensing films. The electronic control was programmed to heat the chips in temperature steps of 4°C, at 24, 28, 32, and 36°C. Thus, if room temperature is between 24 and 28 °C, the chips will be heated to 28°; if it moves above 28°, the chips will step in temperature to 32°. Such a temperature change is much easier to deconvolute from the resistance data than a slow change in temperature as would be found in a spacecraft cabin. Testing was then done at 28° or 32°.

The films were initially tested for response using the data acquisition unit built under a previous program. A unit capable of testing up to four chips, the number chosen for the flight unit, was built early in the program. As the electronics development task progressed, refinements were made to the test unit, until a brassboard of the flight unit was made and provided for all further testing. This data acquisition unit was controlled using a PC computer and a program was written in Labview to control the unit and acquire data. In order to deliver known concentrations of analyte to the sensors, a gas handling system was built and a program for control of the gas handling written in Labview. A schematic of the gas handling system is shown in Figure 3.2. The data acquisition and gas control programs were linked so that time, concentration of analyte in air, humidity, temperature and flow rate were controlled and recorded along with resistance of each sensor at programmable intervals from 10 seconds to one hour.

The air which is used in the gas handling system is cleaned and dehumidified using molecular sieve and desiccant. The cleaned, dehumidified air can be humidified to a controlled level by directing it through a reservoir of distilled water. The gas handling system was built to handle liquid and solid analytes through the use of sparge tubes. The sparge tubes direct cleaned air at a controlled flow rate into the liquid or over the solid; air which is saturated in the analyte then leaves the sparge tube where it is mixed with cleaned, humidified air. By controlling the relative flow rates of air going into the sparger and the carrier air, concentration of analyte in cleaned, controlled humidity air can be selected. Analytes in the gas phase can be plumbed in to the system to bypass the sparge tubes and mixed with cleaned, humidified air.

After the gas handling system was built, using stainless steel valves, glass containment and static mixers, Teflon® and stainless steel compression fittings and Tygon® tubing, it was tested for accuracy of delivery of methanol using a hydrocarbon analyzer which had been calibrated on methanol. Full saturation of the air leaving the sparge tube was

confirmed by sparging air at a known flow rate through ethanol for 12 hours and comparing the weight of ethanol lost over the period with the calculated weight loss. Weight lost was within 2% of the calculated loss.

After several months of using the gas handling system, it was found that the data analysis software routines were quantifying the analytes substantially lower than the presumed delivered concentration, and were reporting single gases as combination. It was also seen that sensor recovery was significantly slower than previously observed. Investigation of the gas handling system showed that the Tygon® tubing used in the plumbing was reacting with the analytes and absorbing some analytes into the walls of the tube. The Tygon® was removed and replaced with Teflon® tubing. Several months of data were rejected as contaminated or possibly contaminated, and the training sets retaken. In addition, a regular schedule of gas system calibration using the hydrocarbon analyzer was instituted.

3.3 Laboratory Test Input to Data Analysis - Training Sets

After the completion of sensor geometry and polymer selection and test phases, two sets of sensor chips were made. Each set consisted of four substrates, with eight sensors each. Four polymer films were deposited on each substrate, to make two sensors of each polymer on the chip. In this way there were 32 sensors made of 16 polymers, so that if any sensor stopped working, there was another sensor of the same material available. Two sets of chips were made; one was arbitrarily labeled "Flight" and the other "Flight Spare" sets.

Training sets for use by the software analysis task were made using both sets of chips. The data from these training sets were used to determine which method or methods of data analysis would be used on the flight data. The training sets were also used to determine the JPL Electronic Nose's limit of detection in this program for each of the target compounds. For compounds with relatively high 1-hour SMACs, such as ethanol (SMAC = 2000 ppm), sensor response was not pushed to the lower limit of detection; a moderate concentration for the gas handling system was selected as the lower limit. Table 3.1 lists the limit of detection for each compound measured, as well as the compound's SMAC.
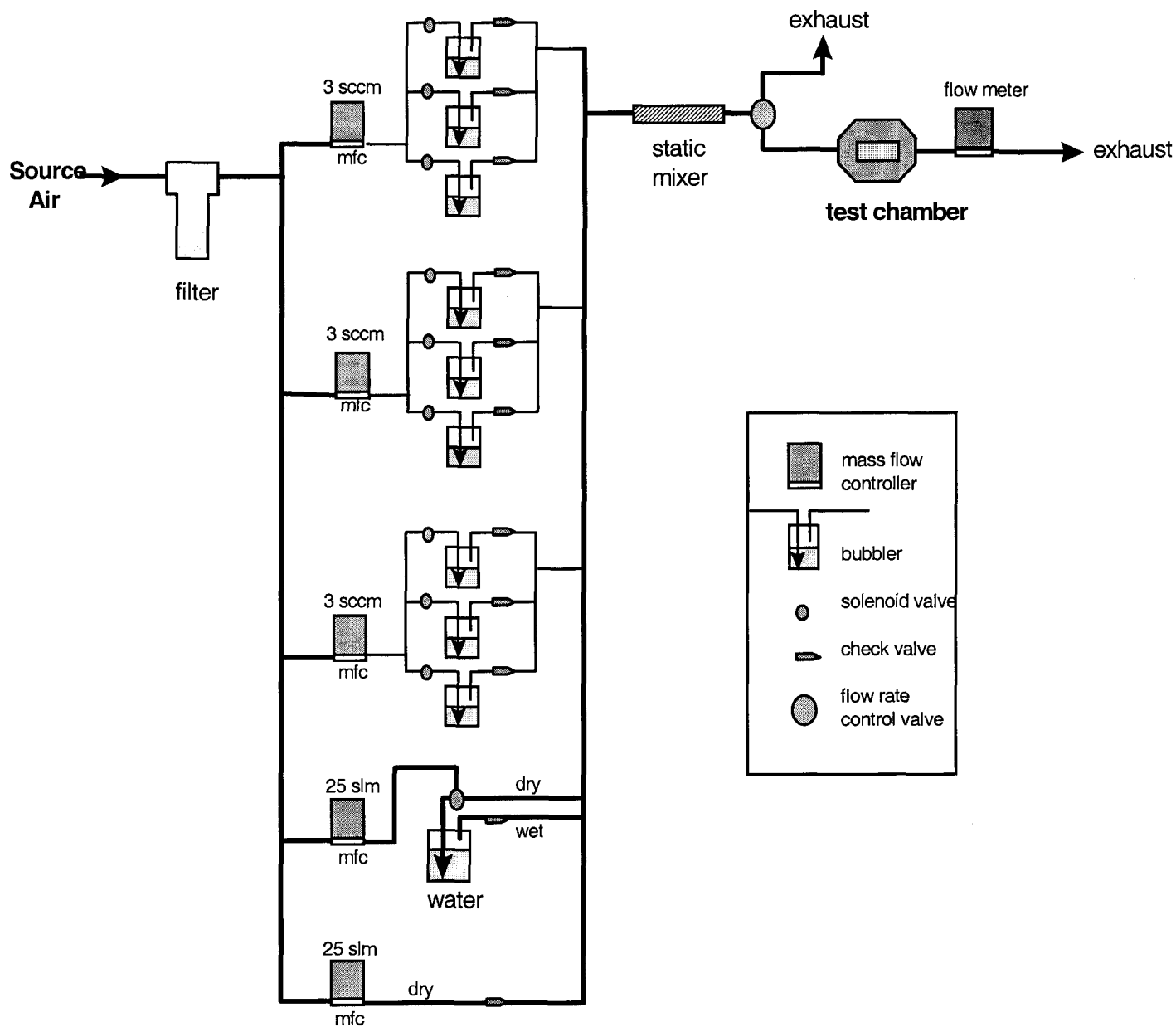
Figure 3.2 *Gas handling system built to be able to deliver combinations of three gases and select humidity and flow rate. Controlled by a PC using Labview.*

The Data Analysis subtask required a database of sensor array responses to use for extracting a signature, or fingerprint, pattern for each gas. The flight and spare chips were exposed a series of gas events requested by the software designer. In this series of events, the sensors were exposed repeatedly to different concentrations of the target compounds. Those data were then used by the Data Analysis task to determine the fingerprints for each gas. A typical single gas event series would expose the sensor array to a series of concentrations of two gases.

Concentrations changes were not organized in either ascending or descending concentrations. The concentration ranges to which the sensor arrays were exposed for each gas is shown in Table 3.1, and a typical single gas exposure event sequence is shown in Figure 3.3. The concentration ranges were determined primarily from the ranges accessible to the gas handling system for each compound, based on the saturated vapor pressure of the compound and the flow rates achievable in the system. Results from early training sets and data analysis are presented in the paper "Monitoring Space Shuttle Air for Selected Contaminants Using an Electronic Nose," presented at the 28th International Conference on Environmental Systems, Danvers MA, July 12-16, 1998. This paper is included in this report as Appendix A.

Table 3.1 *Target compounds for electronic nose shuttle experiment and JPL limits of detection. CO_2 and hydrazine were deleted from the list; see Section 2.*

Compound	Detected on shuttle (ppm) [6]	1hr SMAC (ppm) [7,8]	Detection Limit (ppm)	Testing Range (ppm)
alcohols				
methanol	< 1	30	5	5 - 300
ethanol	.5 - 5	2000	50	10 - 130
2-propanol	.4 - 4	400	50	30 - 160
ammonia	0	30	20	10 - 50
benzene	< .1	10	10	10 - 150
CO_2	320	13000	*	*
indole	0	1	0.03	.006 - .06
hydrazine	0	4	*	*
methane	1 - 10	5300	3000	1000 - 7000
formaldehyde	0	.4	25	25 - 510
Freon 113	.1 - 1	50	20	20 - 600
toluene	.4 - 4	16	15	15 - 60

* compound eliminated from target list; not tested at JPL
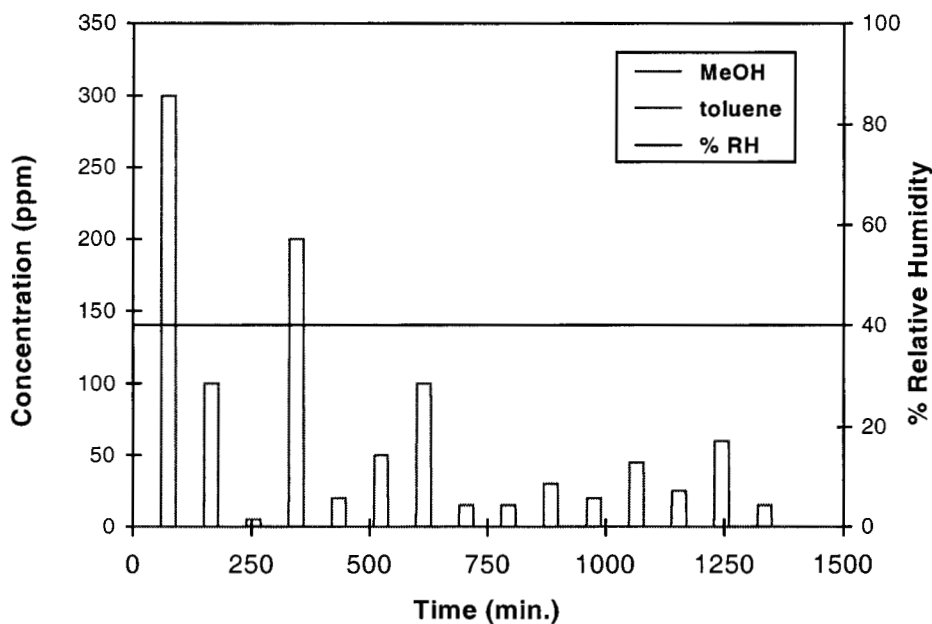
Figure 3.3 *Typical gas exposure event sequence for training sets. Up to three gases can be delivered simultaneously, and relative humidity can be varied. Training events were typically 30 minutes of compound with 60 minutes of clean air between them.*

An exhaustive set of mixed gas training sets was not run because of the time constraints after changing the tubing in the gas handling system (see Section 3.2). The Data Analysis task was provided with data which made it possible to judge the additivity of the gases and the capability to deconvolute the signals. Mixed gas results are discussed in Section 5.3.3.

4. ELECTRONICS DEVELOPMENT: DATA ACQUISITION AND DEVICE CONTROL

Device and data control for the ENose consists of controlling the pneumatic system, the pump and solenoid valve, and interrogating the sensors at a known time and interval. Data acquisition consists of measuring the sensor voltage under known current conditions and converting it to resistance, computing the sensor resistance change, and storing the intermediate and final results onto a flash memory card for ground base analysis. The electronics development task also provided hardware and software for the laboratory testing of sensor substrates and polymer films described in Section 3.

4.1 Computer-Controller
At the beginning of the program, the plan was to fabricate data acquisition and control hardware with memory, and to include a serial port for transfer of the stored data. Early work was done using a desk-top computer for control, and a National Instruments DAQpad to send commands to open and close valves and to acquire resistance data from the sensors by measuring the voltage at a known current provided by the DAQPad. Research into available hardware showed that it would save considerable time and cost to use an off-the-shelf Hewlett Packard 200LX palm-top computer for control. Using this computer for control required designing a circuit to operate the pump and the solenoid valve, and to acquire resistance data from the sensors. The HP200LX can be used with a flash card for memory and is equipped with an infra-red port for data transfer. For this application, the HP200LX was equipped with 6 MB of flash memory and 2 MB of built in RAM, sufficient for 15 days of monitoring. Larger memory can be obtained..

The circuitry designed for use with the HP200LX was fabricated and tested in the laboratory using a desk top or lap top PC for convenience of the operator. The hardware developed for sensor development work was also operated in the laboratory using a desktop computer.

4.2 Power and Clock
Development of the electronics for data acquisition and device control included the ENose power up sequencing and provision of power for the device. The intention at the beginning of the program was to provide power with batteries. The safety and flight qualification issues associated with the use of batteries made it difficult to include them on a shuttle experiment so the orbiter 28 V dc power bus was used to power the device and the computer. Because of safety considerations, the batteries were not used in the palm-top computer. A power supply and circuitry designed and built for this application were used to boot the computer and to transfer the flight software from the flash memory to RAM.

The computer is able to keep accurate track of time elapsed, but there was no way to record the time of turning on the device except by manual recording by a crew member. To avoid having to depend on a crew member for accurate timekeeping, a real-time clock was added to the device, so that when the HP200LX was turned on, the clock

would set the time in the computer. The real-time clock was set at JPL before delivery to JSC. One LiSOCl$_2$ battery was included in the device, to power the real-time clock.

4.3 Sensor Substrate - Co-fired Ceramic Chips

As discussed in Section 3.1, a gas sensor test chip was designed to allow experiments with sensor size and geometry, in order to determine the best combination of size and geometry for this application. The design of the test chip and its original circuit placed each sensor on the chip sequentially in the feedback loop of an operational amplifier using multiplexing circuitry. Five requirements were met in the design:

a) Common bussing was used to conserve pins

b) Kelvin voltage sensing was used in the surround circuitry to avoid analog switch resistor voltage drops

c) Electrode guarding was used to eliminate leakage currents between sensors.

d) All sensors except the one being interrogated were grounded.

e) Structural geometry variations were used to separate contact and sheet resistance

The first four characteristics were kept in the flight chip design.
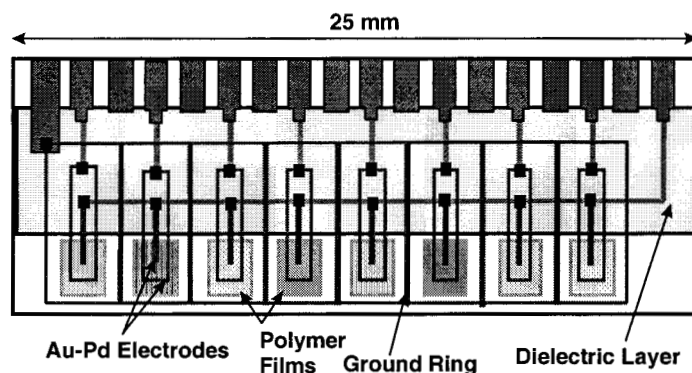
Figure 4.1 Design of the flight chip with 8 U-bend electrode sets in Au-Pd. The unwired terminals on the chip go to RuO$_2$ heaters and the controlling/reading thermistor on the back of the alumina substrate

It was found that the co-fired ceramic technology used to make the sensor substrates could result in pinholes in the insulating glass, especially at the vias, and the method of depositing polymer solutions would then result in cross-talk between sensors. In addition, in some cases, polymer could bridge the space between sensors. To avoid cross talk, two approaches were taken: The design of the sensor was changed slightly to move the vias up into a region where solution would not touch them, and grounding rings were placed around all sensors to ground any current flowing between sensors. Further work in sensor film development led to depositions which did not bridge, and work with the substrate fabrication process led to pin-hole free chips, but the grounding rings were kept as a safety measure. The design of the substrate used to make the flight unit sensors is shown in Figure 4.1.

4.4 Data Acquisition Circuit

At the outset of this program, it was clear that an approach to data acquisition that would be capable of resolving resistance changes on the order of 1 in 10^5 or 1 in 10^6 would be necessary. As the relationship of resistance change to gas concentration was not known at the beginning of the program, the data acquisition task assumed that the most difficult case would be that 10 ppm change in gas concentration would translate to 10 ppm resistance change. In addition, as the task was to miniaturize the entire system, an approach to measurement that did not require extensive instrumentation as well as an approach that would be cost effective for this program was necessary. In practice, the typical resistance change for 10-50 ppm of contaminant is on the order of 2×10^{-4} (200 ppm resistance change), and and may be as small as 1×10^{-5} (10 ppm resistance change).
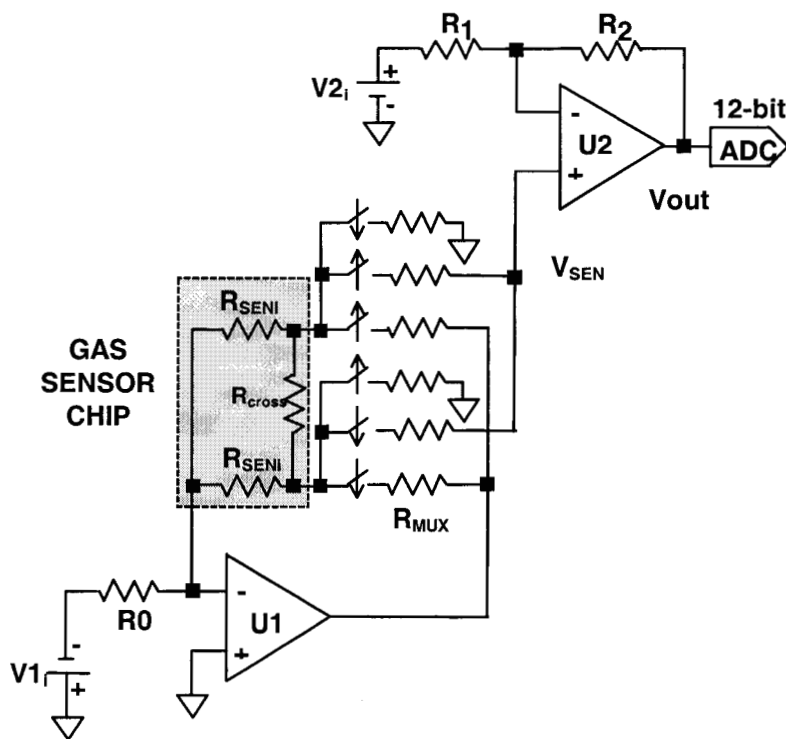
Figure 4.2 *Breadboard: 12 Bit Dual Offset Nulling Amplifier*

Small changes in resistance are measured using a 12 Bit Dual Offset Nulling Amp, in which a known current is put through the sensor resistor Rx_i by $V1_i$ and fixed resistor R0. The resistance measurement breadboard circuit diagram is shown in Figure 4.2. It is designed to allow the measurement of film resistance changes as 1 in 10^5, to eliminate cross talk between sensors, and to minimize sensor chip pin count. The current setting voltage for each sensor, $V1_i$, is determined by a 12-bit binary search in the range of 0-2.5V. The search is performed by setting $V2_i$ and $V1_i$ to approximately midrange, and determining whether the output, V_{out}, is high or low with respect to $V2_i$.

$V1_i$ is ranged higher or lower for 11 additional steps so that the U2 voltage (V_{out}) approaches the linear region of U2. This ensures that the output of U1 is within its linear range. Subsequently, $V2_i$ is ranged in a smiliar manner with $V1_i$ fixed so that V_{out} is within the linear range of U2. With the circuit operating in this linear fashion, R_{SEN} can be determined.

The voltage across the sensor is determined with precision by subtracting $V2_i$ from V_{SEN}. The difference is then multiplied by a fixed gain, $(R_2/R_1) + 1$, where R_2 and R_1 are fixed resistors. For each measurement, the DACs and ADC are locked to the same voltage reference, where DAC is Digital to Analog Converter (12 Bit MAX538 and MAX539), and ADC is Analog to Digital Converter (12 Bit LTC1286).

The architecture of the sensor substrate, the shaded region in Figure 4.2, indicates that one side of each sensor, R_{SENi} is connected to a common node which is connected to the inverting input terminal of Operational Amplifier U1. Resistance caused by cross-talk and not by polymer bridging, R_{cross}, is eliminated by grounding all unused sensor nodes on either side of the sensor under test. This feature became unnecessary as sensor development proceeded, but it was not removed from the circuit.

In practice, detection of changes in polymer resistance of 1 in 10^5 was achieved. The ENose circuit implementation is unique in that the circuit works with the HP200LX in the loop. Since the resistance changes are relatively slow, $V1_i$ and $V2_i$ data for each sensor film are stored in microcontroller memory and used for later measurements. Only if V_{out} is out of range are these values redetermined. That is, the HP200LX dynamically checks V_{out}. If V_{out} is out of the linear range of U2, the HP200LX requests the microcontroller to reset $V1_i$ and $V2_i$ to match V_{out} to within the ADC 12 bit resolution. This amplified remainder is digitized with the 12 bit Analog-to-Digital Converter (ADC) and signal averaged 8 times. The reported resistance change has the equivalent of 18-20 bit resolution.

4.5 Device Control
ENose device control was implemented to be as autonomous as possible, to minimize the need for crew interaction in the ultimate design of such a device as an incident monitor. Nevertheless, ample feedback is available to the operator to verify proper operation. Upon power up, the ENose goes through a 60 second power up sequence, which includes self-test, and guarantees a clean reset. During the power up sequence the solenoid is toggled on and off to verify valve operation. The HP200LX then boots, requests the time from the real time clock, and enables the gas flow system pump. Upon verifying the action of all the control parts, the computer commands the ENose microcontroller to find the operating points of the 32 individual sensors. Upon verifying the action of all the control parts, the computer commands the ENose microcontroller to find the operating points of the 32 individual sensors. These operating points are the V1 voltage and the DAC value proportional to the sense current for each sensor. The HP200LX then requests data periodically by serial command. Data are cataloged and tagged, and sensors are rescaled if drift or response makes it necessary. Instrument activity is indicated by LEDs on the side of the enclosure, one for "Power & Measure"

and one for "Baseline". Closed loop temperature control is done by the ENose hardware using an analog feedback loop. (See discussion on need for temperature control in section 3.2).

5. DATA ANALYSIS SOFTWARE DEVELOPMENT

Data analysis is an integral and important step in developing the ENose. Without adequate data analysis, the data acquired by ENose hardware will be meaningless. High-level data analysis tools are needed to deconvolute the gases and gas concentrations from the response patterns across the sensor array. During this program, the data analysis task focused on development of a data analysis method that can correctly identify and accurately quantify a gas event of single or mixed gases.

For an electronic nose system, the task of identifying and quantifying a gas event is roughly a two-step procedure:

> 1) pattern extraction, where the response pattern of a gas event is extracted for further analysis, and

> 2) pattern recognition, where the gas event is identified and quantified on the response pattern extracted.

Before these steps can be taken, a database of expected gases must be compiled; this database was taken in the ENose lab as described in Section 3.3.

The work of designing a series of software routines to go through the steps described below was done using MATLAB, from MathWorks, Inc. Several routines from MATLAB and other sources were used directly or modified for this application. MATLAB is a flexible program, and thus appealing for development of software, but it runs relatively slowly. For future use, where real-time or quasi-real time analysis is desired, the routines can be translated into C and run on a desk top or lap-top computer.

5.1 Response Pattern Extraction
In order to extract the resistance response pattern accurately from raw time-series resistance data it must be pre-processed. This conversion is important because for sensing media such as the conducting polymer/carbon films used in this program, relative response changes have been found to be more reliable than the response shapes. The exact method of extracting the response pattern may be application dependent, but in general it will involve four sequential steps: 1) Noise removal, 2) Baseline drifting accommodation, 3) Gas event occurrence determination, and 4) Resistance change calculation. Figure 5.1 shows the results of pre-processing.

5.1.1 Noise removal A sensor's response to a gas event might be buried in noise, especially at the gas concentrations targeted in this program (1 - 100 ppm). The main source of this noise is response fluctuation in the sensing films. Some polymer films were noisier than others; that noise could have been caused by high sensitivity of the

film to small changes in pressure caused by air flow. Non-uniformities in the film thickness and carbon dispersion could also be responsible for noise. In general, this fluctuation is fast compared to the response to a gas event. It is expected that a less responsive sensing medium will have a larger relative fluctuation. The first step in the preprocessing is therefore to filter out this high frequency fluctuation using appropriate digital filtering.

The method for noise removal used here is zero-phase forward and reverse digital filtering. The length of the filter may be different for different sensors and can be determined by trial and error. Figure 5.2 shows a representative result of the effect of this filtering to one sensor.

(a)   (b)
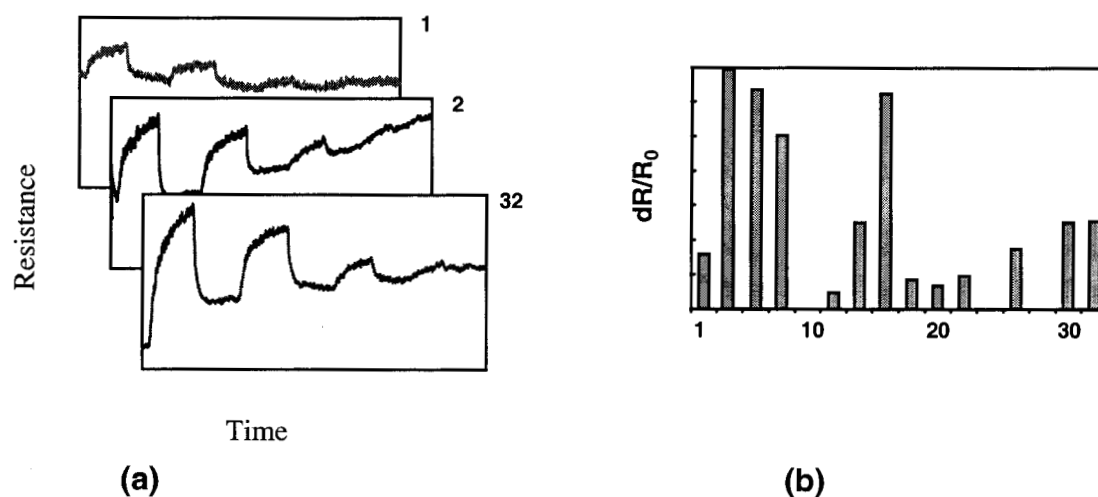
Figure 5.1 *Preprocessing converts the recorded time-series resistance data shown in (a) to resistance response pattern, shown in (b).*

5.1.2 Baseline drift accommodation   Baseline drift is one of the most difficult problems to be solved in analyzing Resistance vs. Time data from the ENose. The causes for the baseline drift can be multiple, and include variations in temperature, humidity, or pressure, aging of the sensors, and sensor saturation. However, there is at present no clear understanding of the underlying mechanism of any one of the causes, which makes drift compensating attempts very difficult.

In general, the baseline drift is slowly-varying in nature compared to the response time of a detectable gas event, whether the drift is caused by temperature, pressure or humidity variations, or some other cause. This difference in time scale enables the use of a long-length digital filter to determine the approximate baseline drift and then subtract it from the raw data. Figure 5.3a shows the baseline drift determined in one sensor; Figure 5.3b shows the result of processing the data by with both high and low frequency filters. Although this will not accommodate the drift totally, it will eliminate the effect to a manageable degree.
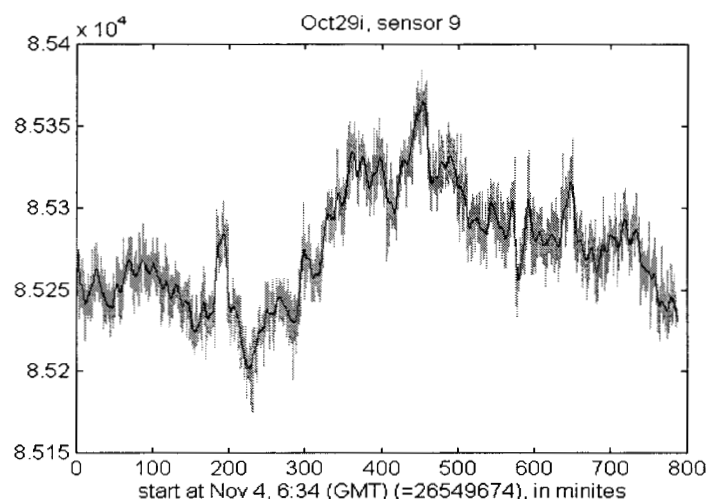
Figure 5.2 *Green line: raw resistance recorded. Red line: smoothed resistance*

5.1.3 Gas event occurrence determination   A scheme for automated determination of whether and when a gas event occurs has been developed. It is based primarily on threshold calculation, in which the resistance change over a certain time interval is calculated, and a time-stamp is registered if the change exceeds a pre-set threshold. This routine can detect most gas events; however, it was also found that it tends to falsely identify baseline drift or noise as gas events. Consequently, in this experiment, the determination of a gas event in practice was largely done by visual inspection of the events selected by the routine. In this way, effort was focused on gas identification and quantification.

5.1.4 Resistance change calculation   The calculation of the resistance change may not be obvious, because at low gas concentration range the responses do not have consistent characteristic shapes. However, it is expected that different sensors have relatively different response strengths. It is this relative responsiveness which determines the fingerprint of that gas – the response pattern. To preserve this relative responsiveness it is important that the any calculation method of the resistance change should be taken at the same time stamp after the initial presentation of a gas.

5.2 Pattern Recognition - Data Analysis Techniques
Although response patterns such as the one shown in Figure 5.1b can provide hints to identify different gases, more quantitative knowledge can be obtained only with the help of dedicated data analysis tools to identify and quantify detected gases. Various approaches to response pattern analysis and classification have been studied and investigated. Each has its advantages and disadvantages. In the following sections some of the data analysis methods which have been evaluated in this program are reviewed.
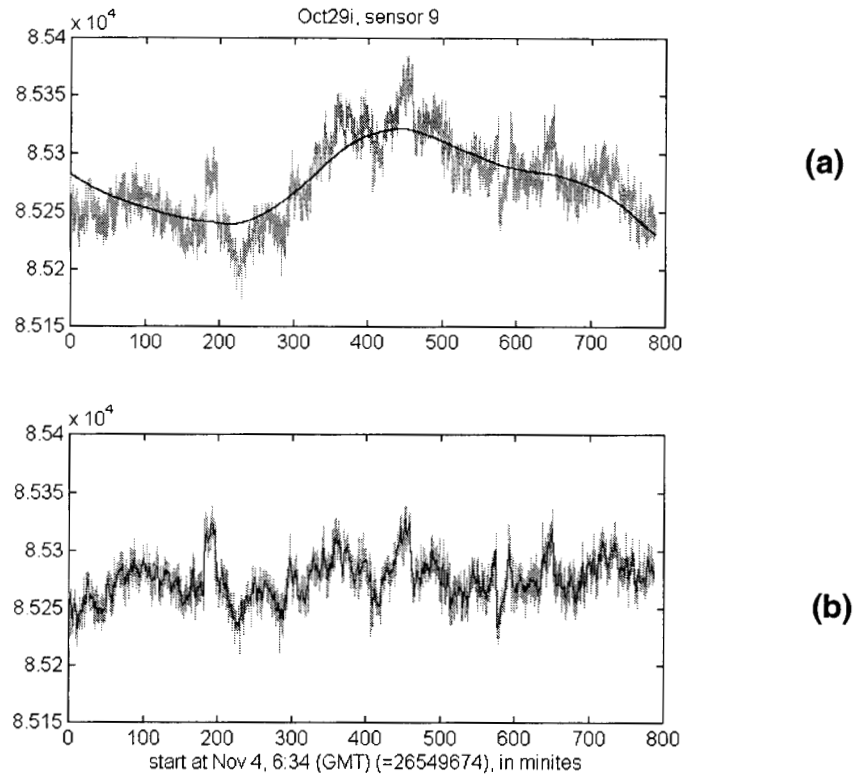
Figure 5.3 *a) Blue line: baseline drift. b) Red line: smoothed and baseline drift corrected resistance*

5.2.1 Principal Component Analysis Principal Component Analysis (PCA) is one of the most widely used methods for electronic noses and other array-based sensors. It performs linear projection of multivariate data sets into a few informative and independent axes. The new axes are the principal components of the data stream, and the separations between data samples are readily visualized in this transformed data space. Nevertheless it is not optimal for classification since it ignores the identity (class label) of the gas examples in the database.

5.2.2 Differential Function Analysis Differential Function Analysis (DFA) is another commonly used statistical approach to analysis of arrays of data. Its goal is to find projections (hyperplanes) that maximize the distance between examples of different groups yet minimize the distance between examples of the same groups. Compared to PCA, DFA tends to do better with a projection that contains subtle, but possibly crucial, gas-discriminatory information, while PCA may do better with a projection that contains high-variance random noise. Unlike PCA, DFA looks at the class label of each example and is therefore more appropriate for classification purposes.

5.2.3 Neural Networks   Neural Networks (NN) are another popular approach to data analysis for array based sensors. Neural networks can be taught to simulate any function. For this application, NN software would try to find a best-fit function (linear or nonlinear; no models needed) that takes relative resistance changes as inputs and outputs the gas classification. NN is good for generalization of functions to cases outside the training set and is more suitable than DFA when the sensor signatures of two gases are not separable by a hyperplane (*e.g.* one gas has a signature surrounding the signatures of another gas.) NN generally requires "clean" training data and is therefore less amenable to noise or drift in the training data than most other approaches. NNs are inferior to DFA in classifying data sets which may overlap.

5.2.4 Linear Algebra   Neither DFA nor NNs are well suited to recognizing the sensor signatures from combinations of more than one gas. For this scenario, one can use a linear algebra (LA) based approach. LA tries to solve the equation $y=Ax$, where vector y is an observation (a response pattern), vector x is the cause for the observation (concentrations of a gas or combinations of gases), and matrix A describes system characteristics (gas signatures obtained from training data). There are two ways to solve the equation: direct method or matrix pseudo-inverse, and least-squares fitting method. For ENose data analysis where the response pattern can be noise corrupted, so there may exist no exact solution, the least-squares fitting method is preferred. Among NN, DFA, and LA, LA has been found to perform best; however, LA is suitable only if the training data are linear.

5.2.5 Differential Evolution   Differential Evolution (DE) represents some recently emerged so-called genetic algorithms. It is a parallel direct search optimization tool. It begins with an initial randomly-chosen population of parameter vectors, adding random vector differentials to the best-so-far solution in order to perturb it. A one-way crossover operation then replaces parameters in the targeted population vector with some (or all) of the parameter values from this "noisy" best-so-far vector. In essence it imitates principles of genetics and natural evolution by operating on a population of possible solutions using so-called genetic operators, recombination, inversion, mutation and selection. Various paths to the optimum solution are checked and information about them can be exchanged. The concept is simple, the convergence is fast and the required human interface is minimal: no more than three factors need be selected for a specific application. However the last advantage is also its disadvantage: limited control for ENose data analysis.

5.2.6 LM Nonlinear Least Squares Method   For nonlinear models the technique of choice for least-squares fitting is the iterative damped least-square method of Levenberg and Marquardt, hereafter referred to as LM-NLS. Similar to LA, LM-NLS tries to find the best-fit parameter vector x from an observation vector $y,$ which is related to x through a known linear or nonlinear function, $y=f(A,x)$, *e.g.* $y=A_1x+A_2x^2$, where A_1 and A_2 are system characteristics obtained from training data. This method begins from a given starting point of x, calculates the discrepancy of the fit:

$$residual = (computed-observed)/\sigma,$$

where σ is the standard deviation, and updates with a better-fitted parameter **x** at each step. LM-NLS automatically adjusts the parameter step to assure a reduction in the residual: increase damping (reduce step) for a highly nonlinear problem, decrease damping (increase step) for a linear problem. Because of this ability to adjust damping, LM-NLS is adaptive to both linear and nonlinear problems and is the data analysis method used in this ENose program.

5.3 Sensor Characterization and Calibration

Whatever the method selected, before it can be used to analyze unknown gas events, it must be trained or calibrated. Sensor characterization and calibration, first and foremost, provides the basis for later accurate identification of the gas type and quantification of gas concentration. It also provides important feedback information for the selection and development of the data analysis method itself.

During this ENose project, lab training data of known compounds at known concentrations of about 550 gas events of single target gases and several pairs of mixtures have been collected. The following summarizes what has been observed with these data.

5.3.1 Single gas responses In the course of this work, it was found that the response of the films to the target compounds is linear with concentration only within a limited range. The tests done in Prof. Lewis' lab were done at substantially higher concentrations than the SMACs for this program, and found responses to be linear. The data analysis approach used in Prof. Lewis' work relies on linearity, and could not be used here. The nonlinearities in the training data generated for this program appear to be of low order, but successful identification and quantification of gas events must take the nonlinearities into account. Figure 5.4 shows the sensor responses vs. concentration to a single gas, ethanol.

To obtain sensor characteristics without further knowledge of sensor nonlinearities, a second order polynomial fit was used to model the nonlinearities. For each sensor response to each gas, the program finds the best-fit coefficients **A₁** and **A₂** (in the least-squares sense) to the following equation:

$$resistance\ change = A_1 C_g + A_2 C_g^2$$

where C_g is gas concentration. The fit is constrained to pass through the origin. **A₁** and **A₂** are 13x13 matrices characterizing the sensors' response to ten targeted gases plus water, humidity change, and the propanol wipe.

5.3.2 Single gas response patterns Because of the nonlinearity of response with concentration, there is no single signature or fingerprint for one gas at all concentrations. In general, the response patterns for one specific gas remain similar for the concentration range of interest. Figure 5.5 shows representative response patterns for all sensors to the ten target gas compounds at a median concentration level.
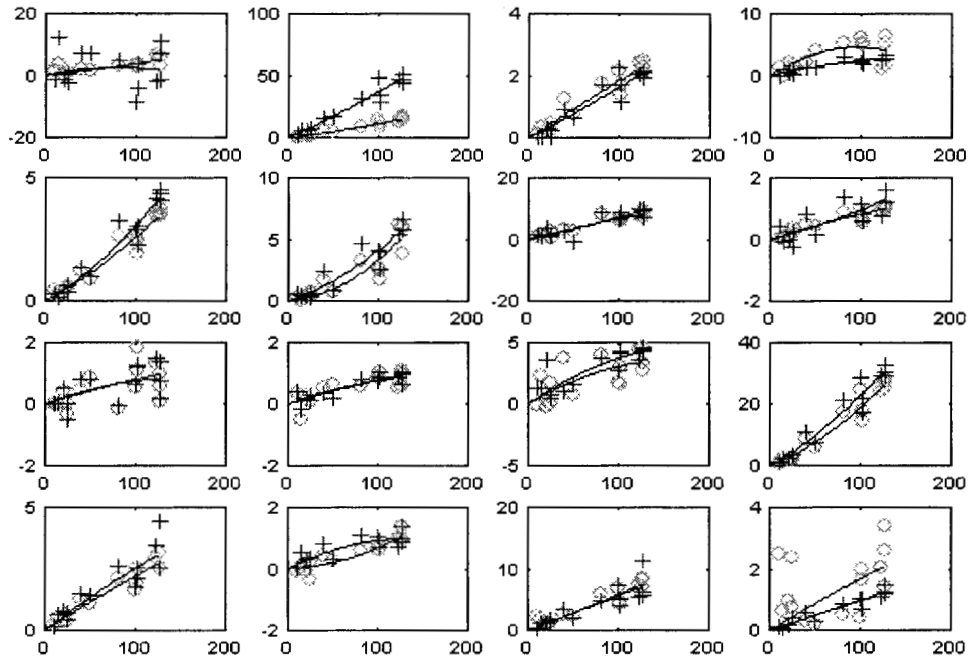
Figure 5.4 Sensor resistance changes (vertical axis) vs. gas concentrations (horizontal) for ethanol. One pair of sensors in each subplot. Low-order nonlinearity was observed. "+" and "o": experimental data points; lines: least-squares fitting curves

It is clear from the signature patterns in Figure 5.5 that similar response patterns were observed for some different gases. For example, ethanol and methanol have similar signature patterns. Regression analysis also pointed out linear dependency to certain degrees. This means that signature pattern of one gas could be expressed as a linear combination of the response pattern generated by some other target gases. To reduce this similarity, the sensors' raw resistance responses must be modified by different weights in the data analysis procedure.
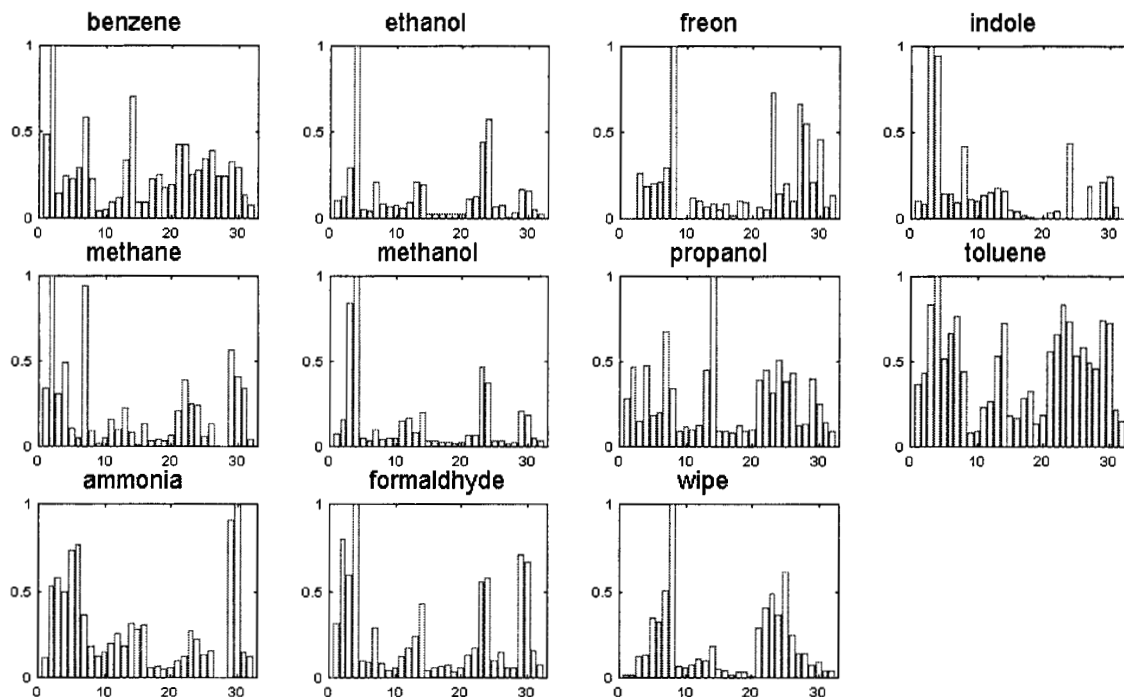
Figure 5.5 *Representative signatures of ten targeted gas compounds plus wipe generated by ENose sensors. Notice the similarity between ethanol and methanol.*

5.3.3 Mixed gas responses Deconvolution for identification and quantification of mixtures relies on the additivity of the sensor responses. Here, *additivity* means that the strength of the response to mixtures of gas **A** at level *cA* and gas **B** at level *cB* equals the response of gas **A** at level *cA* plus the response of gas **B** at level *cB*; (cA + cB) = cA + cB. An exhaustive set of gas pairs was not run because of time constraints after re-plumbing the gas-delivery system with PTFE tubing, so it was necessary to test the additivity of gas pairs on a selected group of mixtures. For this relatively small pool of data, additivity holds for the gas combinations run: ethanol + formaldehyde, ethanol + ammonia, ammonia + benzene, methanol + toluene, methanol + benzene, benzene + propanol, benzene + methanol, as shown in Figure 5.6.

5.4 Software Development Results

5.4.1 Training-data analysis Initial software design focussed on using Principal Components Analysis and Linear Algebra for identification and quantification of compounds. These methods were adequate, but not optimum to the task. The data reported in the paper found in Appendix A were analyzed using those methods, and it was through analysis with PCA and LA that the problems in the Tygon tubing were found. After changing out the Tygon tubing, and new training sets were run, possible approaches to data analysis were reconsidered to check on linearity.

The LM-Nonlinear Least Squares method was chosen for ENose data analysis because it had a higher success rate for identification and quantification than any other methods

that were explored for this application. Here "success" means correctly identifying target compounds and quantifying them to +/- 50%.

For lab-controlled gas events, the overall success rate reaches ~85% for targeted singles and about ~60% for mixtures. Broken down into individual singles or mixture pairs, the success rates for singles are listed below in Table 5.1. The concentration ranges for each single gas are also given. Lower concentrations listed in Table 3.1, where the detection limit at JPL is listed, were done early in the program with PCA and LA analysis.

Table 5.1 *Identification and quantification success rates for single gases. The ranges shown here are ranges used in LMNLS analysis.*

Compound	Concentration Range (ppm)	Success Rate (%)
Ammonia	10 - 50	100
Benzene	20 - 150	88
Ethanol	10 - 130	87
Freon 113	50 - 525	80
Formaldehyde	50 - 510	100
Indole	.006 - .06	80
Methane	3000 - 7000	75
Methanol	10 - 300	63
Propanol	75 - 180	80
Toluene	30 - 60	50

Considering that the raw data are often very noisy at low concentrations, nonlinear at high concentrations, highly correlated in some cases, and weakly additive in some mixtures, these results demonstrate that the LM-NLS method is an effective technique for analysis of an array of sensors. Future work on the ENose will attempt to remove many of the impediments to data analysis, with focus on noise and correlation.

5.4.2 Data Analysis Software Results The ability of the data analysis software to identify and quantify single and multiple gas events in clean air was tested in the laboratory. The targeted concentrations range for quantification was 30% to 300% of the one hour SMAC for each compound. As can be seen from Table 3.1, in some cases it was possible to identify and quantify substantially below the 30% concentration; however, in a few cases quantification was successful only as low as 100% of the one-hour SMAC. In one case, that of formaldehyde, we were unable to reliably identify and quantify below several times the one-hour SMAC. Identification and quantification of single gases at the one-hour SMAC level was successful. Figures 5.7 and 5.8 show some results of single gas identification and quantification graphically.
Single gas identification and quantification done using PCA is shown in the Figures with the paper found in Appendix A.
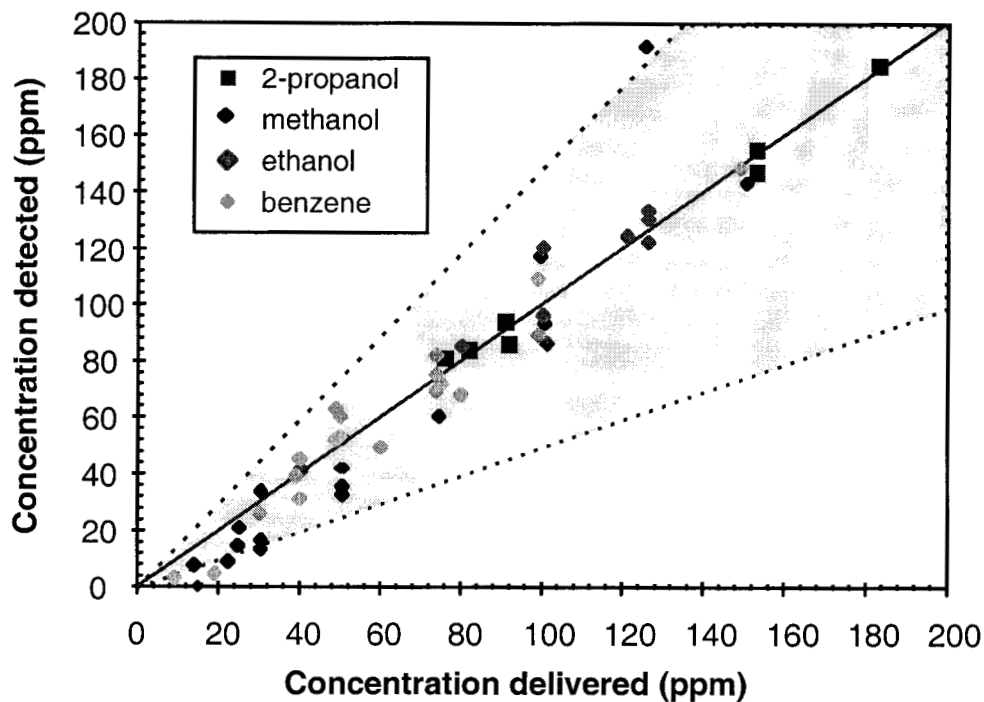
Figure 5.7 *Identification and quantification of four single gases using LM-NLS. The shaded area is the target +/- 50% detection range.*

An exhaustive set of multiple gases was not run; the software design was such that testing several groups would be sufficient to test the ability of the software to deconvolute mixtures. Identification and quantification of mixtures in clean air was moderately successful. Additive linearity holds for some combinations in concentration ranges near the SMAC level of the lower SMAC-compound. The success rate for double gases was somewhat less than that of single gases, as would be expected. Figures 5.9 and 5.10 show the results of double gas identification and quantification.
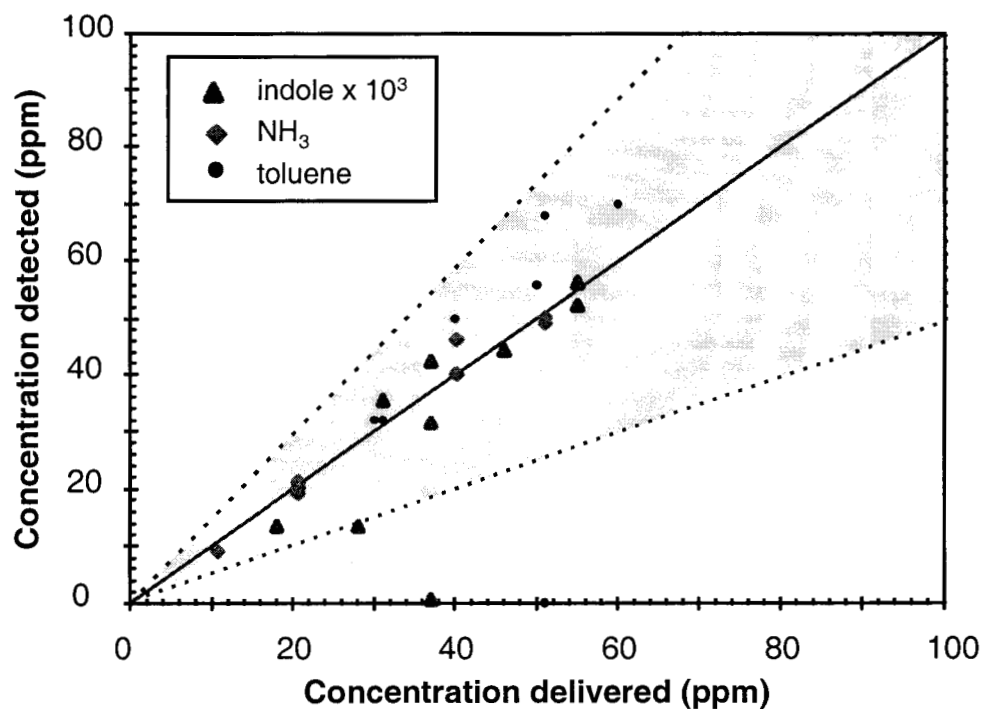
Figure 5.8 *Identification and quantification of three single gases using LM-NLS*
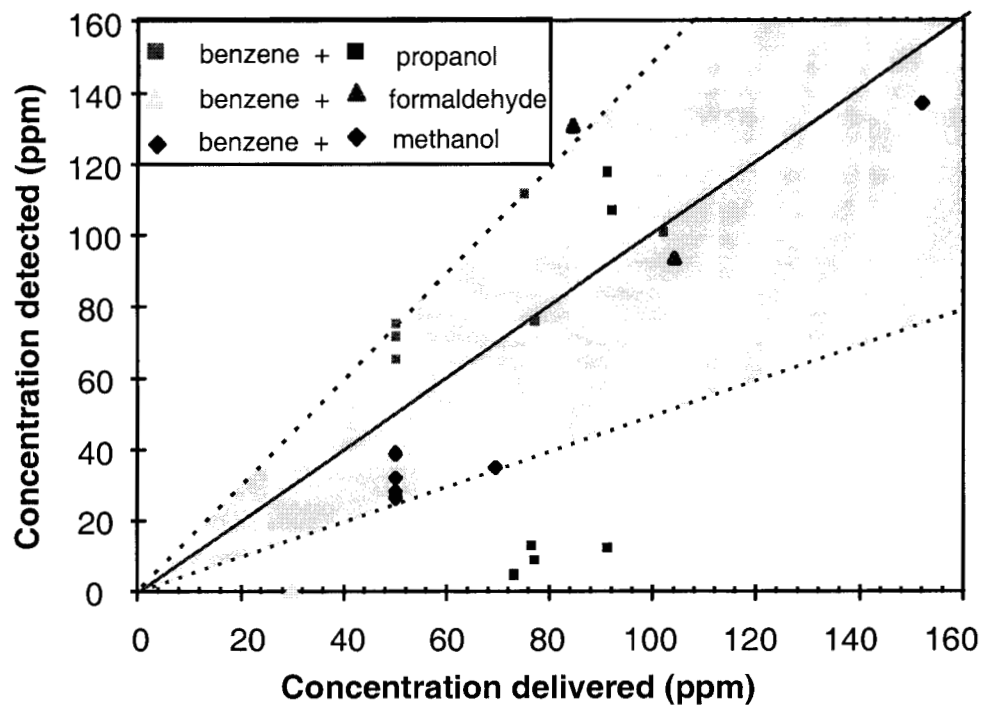
Figure 5.10 *Identification and quantification of sets of double gas; benzene plus propanol, methanol or formaldehyde. Benzene and propanol have very similar patterns in the concentration range of interest and so are difficult to deconvolute.*
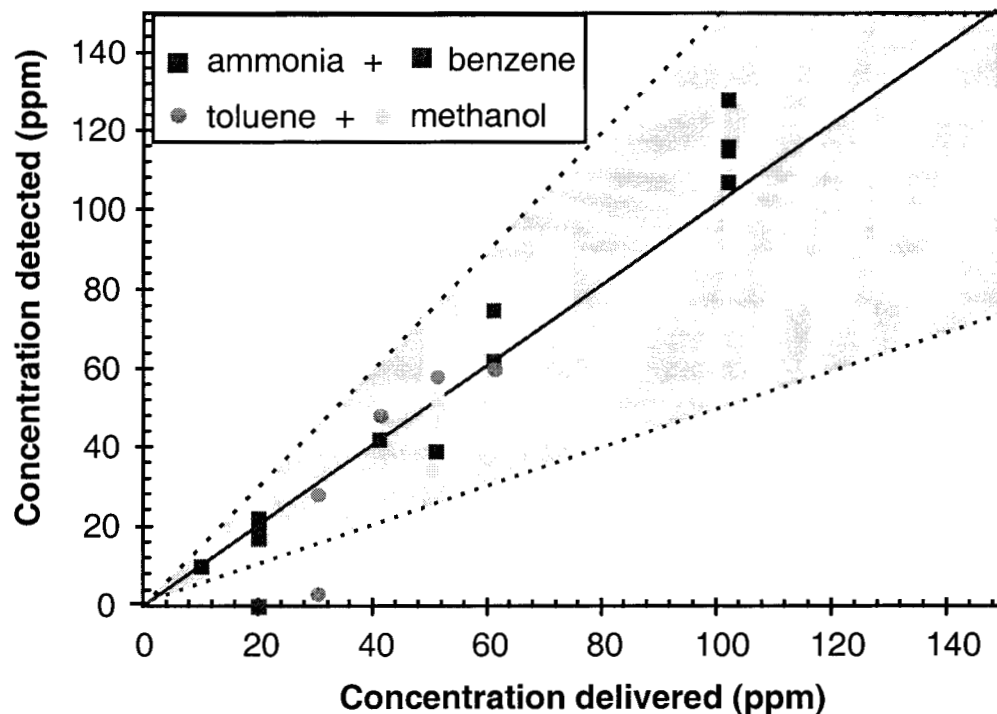
Figure 5.11 *Identification and quantification of sets of double gas; ammonia plus benzene and toluene plus methanol. Nonlinear analysis is necessary for this range of concentrations.*

6. COORDINATION WITH JSC

The task of coordinating the flight experiment with JSC was ongoing, and began immediately upon starting work on this program. Coordination with JSC involved the Toxicology Branch, which participated in the experiment, Krug Life Sciences (later Wyle Laboratories) for Integration Engineering, JSC QA organization, Safety and Mission Assurance, JSC Mission Project & Integration, and training the crew to perform the experiment. At the beginning of the program, the ENose experiment was designated as a Detailed Test Objective (DTO). JPL's interface was then limited to the Krug integration team and the JSC Institutional Review Board (IRB). IRB was issued in May of 98. Eventually, the classification of the experiment was changed to a Secondary Payload. At that point, JPL interface with JSC intensified and was managed by the office of Mission Projects & Integration.

6.1 Toxicology Branch
Immediately upon starting work on this program, coordination with Dr. John James, Chief of the Toxicology Branch at JSC commenced. Early discussions with Dr. James established the utility of the list of target compounds for detection, which had been selected from literature published by Dr. James. Discussions of how to control the experiment led to establishment of collaboration with Dr. James, in which the Toxicology Branch provided Grab Sample Containers for daily air samples during flight

and ground analysis of the contents of the containers. Dr. James was included in the flight experiment as co-investigator.

Further discussions resulted in the decision not to include real time data analysis or data display during flight. A previous experiment with air quality analysis had led to false positive identifications of contaminants, and in order to avoid a similar problem, it was decided to do all data analysis on the ground, post-flight.

Throughout the course of this work, Dr. James and Dr. Thomas Limero of Wyle Life Sciences were included in discussions of the lab work and kept abreast of developments in the sensors.

6.2 Early Human Test Experiment

In January, 1997, the opportunity to test an engineering development model of the ENose during Phase IIA (60-day experiment) of the Lunar-Mars Life Support Test Project was made available to the ENose project by the Crew and Thermal Systems Division at JSC. This experiment provided the opportunity to observe the operation of the sensor chips, to determine how much interference from daily events could be expected, and to confirm the stability of the sensors over time. (*Note: The Lunar-Mars Life Support Test Project was previously called the Early Human Test Initiative, and the chamber called the Early Human Test Chamber, so references to this experiment are made under those names.*)
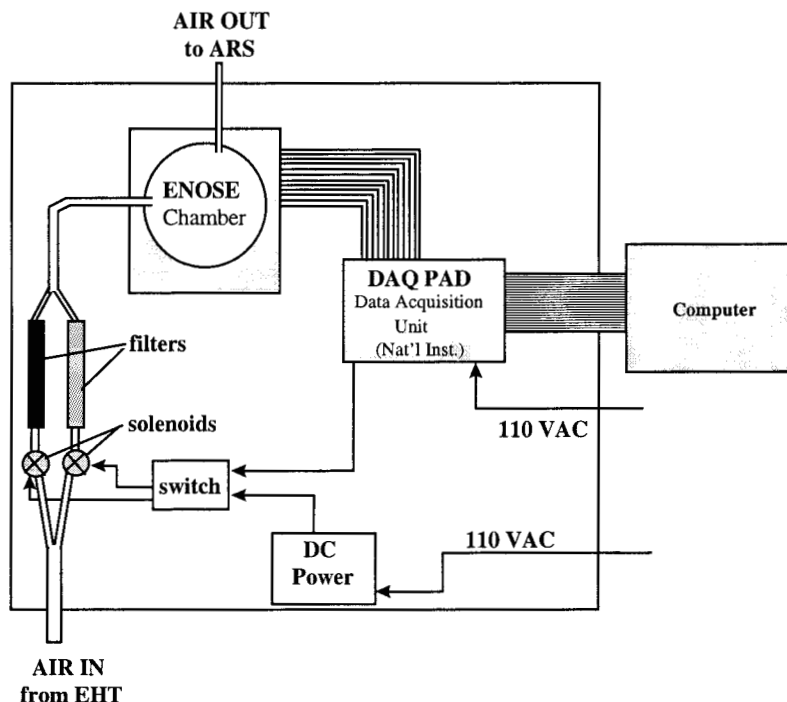

Figure 6.1 *Design of the Engineering Development Model ENose used in EHTC*

An engineering development model of an electronic nose was fabricated at JPL and plumbed in to the air revitalization line of the Early Human Test Chamber (EHTC) at NASA-Johnson Space Center for 49 days in early 1997. Flowing air (0.25 L/min) was taken from the slipstream exiting the EHTC and directed into the ENose system. The air, which had been heated to 30 - 34°C for EHTC testing purposes, was directed either through an activated charcoal filter, put in line to provide clean air baseline data, or through a dummy glass filter, put in line to provide a pressure drop similar to that of the charcoal filter. Solenoid valves were programmed to open the valve to the charcoal filter and provide 30 minutes of clean air flow every four hours; otherwise, the air went through the glass filter. Air then entered the glass enclosed sensor head chamber where resistance was measured every 30 seconds, and then left the ENose system to enter the air revitalization system of the EHTC.

The experiment was controlled using a personal computer and a National Instruments DAQPad. The DAQPad sent commands to the solenoids to open and close and acquired resistance data from the sensors by measuring the voltage at a current provided by the DAQPad.

The design of the engineering development model used in this experiment was somewhat different from that used in the flight unit, as it was early in the development program. A schematic of the unit is shown in Figure 6.1.

The primary results of this experiment were confirmation that the sensor films are stable for several months (measurement one year after fabrication showed the baseline resistance of the films to have changed only by a few percent), that the sensors are sensitive to changes in the atmosphere and can be used as incident monitors to offer early warning of leaks, and that the temperature of the sensors must be controlled to prevent excessive baseline drift.

Figure 6.2 shows ENose response to a spill of trimethylamine (TMA) in the shower/toilet area of the EHTC. The significance of this figure is twofold. Comparison of the time of the crew report of the odor shows that the ENose recorded the change in air quality some 30 minutes before the crew report. Taking into account that the crew probably did not report the odor immediately, it can be judged qualitatively that the ENose recorded the odor several minutes before the crew was aware of it. The second piece of significant information in this figure concerns the baselining, or reference cycle. The reference cycle turned on in the middle of the TMA event. When the reference cycle turned off, a "virtual peak" of the odor change was created. This "virtual peak" makes it possible to deconvolute a slow buildup of contaminant, which might otherwise be interpreted as baseline drift.

This experiment and other results are discussed further in the paper "Monitoring the Air Quality in a Closed Chamber Using an Electronic Nose," presented at The 27th International Conference on Environmental Systems in Lake Tahoe NV, July 14-17, 1997. The paper is included in this report as Appendix B.

6.3 Flight Manifest and Flight Qualification

The Electronic Nose Flight Experiment was originally planned as a Detailed Test Objective (DTO) on STS-91, a Mir Docking Flight in May, 1998. Coordination with JSC Shuttle Integration engineers and with the Toxicology Branch started immediately after the program began. Delivery of the flight unit was scheduled for February, 1998. In February, 1998, when JPL was ready to deliver the unit, the experiment was rescheduled for STS-95, in October, 1998, so delivery was postponed until May, 1998. To enhance the probability of remaining on the manifest, NASA Code U worked to change the classification of the experiment from a DTO, which is easily removed form the manifest, to a payload. Subsequently, with the help of the Mission Project & Integration office, the ENose was classified as a secondary payload, greatly enhancing the chances for a successful manifest. However, the classification change also changed the requirements and required JPL, Wyle, and JSC to perform additional tests and enhance the flight qualification action.

Testing to pass all flight qualification and safety gates was conducted at JPL and at JSC. The ENose met all JSC requirements for a mid-deck payload. The tests and certifications included:

a.   Institutional Review Board (IRB)

b.   Vibration

c.   EMI-RFI

d.   Acoustic

e.   Temperature cycling

f.   Heater analysis for safety

g.   Safety analysis and approval of the real-time clock Li-ion battery

h.   Toxicology approval for the safety of all outgassing of all components

i.   Toxicology approval for the safety of the polymer materials

j.   Certified by JPL Structures and Materials Review Committee (SAMRC)

k.   JSC safety approval
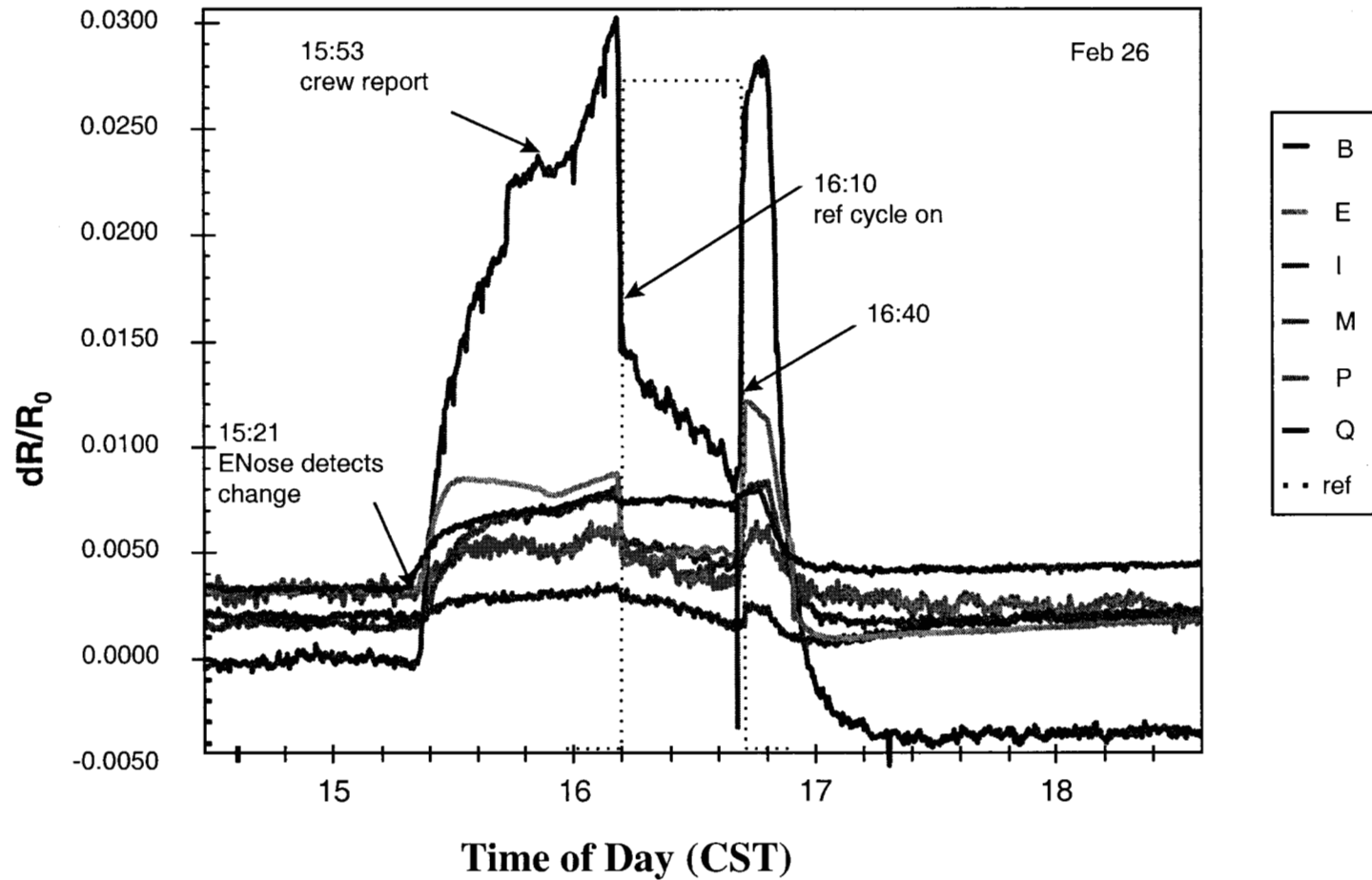
Figure 6.2: *Response of ENose to trimethylamine spill. The ENose can provide an early warning of leaks or malfunctioning equipment in the habitat and can detect slow buildup of contaminants by baselining: at 15:21 the ENose detects abnormal air quality, and crew reports an odor of trimethylamine 30 minutes later; at 16:10 air filtering begins for the reference cycle (baseline); at 16:40 the reference cycle turns off and peaks created by contaminated air allow detection of slow buildup of contaminants*

6.4 Experiment Definition and Crew Training

The ENose flight experiment was designed to provide continuous monitoring of the air in the mid-deck of the orbiter (*i.e.* data points every 30 seconds). The ENose sensor responses to the air was recorded for 6 days during the STS 95 flight (Oct. 29 through Nov. 7, 1998). In order to confirm that the ENose was operating, a crew member would check the operating lights (LEDs) on the side of the unit daily, and provide an "event" or daily marker by exposing the inlet of the unit to an alcohol wipe made of 70% 2-propanol, balance unknown. At the start of the daily check, before exposing the sensors to the wipe, the crew member took a daily air sample in a grab sample container (GSC).

JPL and JSC developed the crew procedure and timeline. JPL researchers met with the crew twice before flight, once as a video conference to familiarize the crew with the objectives of the experiment, and once at JSC to review, practice, and demonstrate the procedures for the experiment.

The crew protocol for the flight experiment was defined to consist of the following steps:

1. ENose deployed in mid-deck 1-2 days after launch (10 minutes)
    a. Remove device from locker
    b. Fix device to its space on top of mid-deck lockers with Velcro strips.
       Space was on mid-deck lockers near an air-intake
    c. Connect pre-routed 28 V power cord
    d. Turn on device and confirm that turn-on sequence is complete:
       LEDs light, computer signature tone and pump can be heard
    e. Log time and comments

2. Daily air samples (grab samples) taken for post flight analysis at JSC (5 min/day)

3. Daily calibration of ENose to 2-propanol done by crew member (5 min/day)
    a. Determine that device is not in a reference cycle (template provided)
    b. Confirm that air inlet screen is not clogged with debris. Clean if necessary.
    c. Open propanol wipe and hold near air inlet 30 seconds. Observe LEDs.
    d. Log time and comments

4. Turn off and stow ENose after experimental period (5 minutes)

The experimental procedure used by the crew is included as Appendix C.

After the flight the GSC air samples were returned to JSC for analysis, and the ENose unit was returned to JPL for data analysis and post-flight calibration on the unit. The ENose was calibrated post-flight to confirm that the sensor baseline resistances and array responses had not changed. After both JSC and JPL analyzed the data, the two teams met for a data review.

6.5 STS-95 Flight Experiment

The ENose flew on STS-95, which launched on October 29, 1998. The flight experiment took place over a period of 6 days, as planned, with no unusual events. The data and unit were returned to JPL after the flight without incident.

7. FLIGHT UNIT DESIGN AND FABRICATION

The design of the flight unit was undertaken early in the program, but many aspects of the design were added as the development tasks proceeded. A diagram of the ENose flight unit is shown in Figure 7.1. Photographs of the flight unit are shown as Figures 7.2 - 7.4.
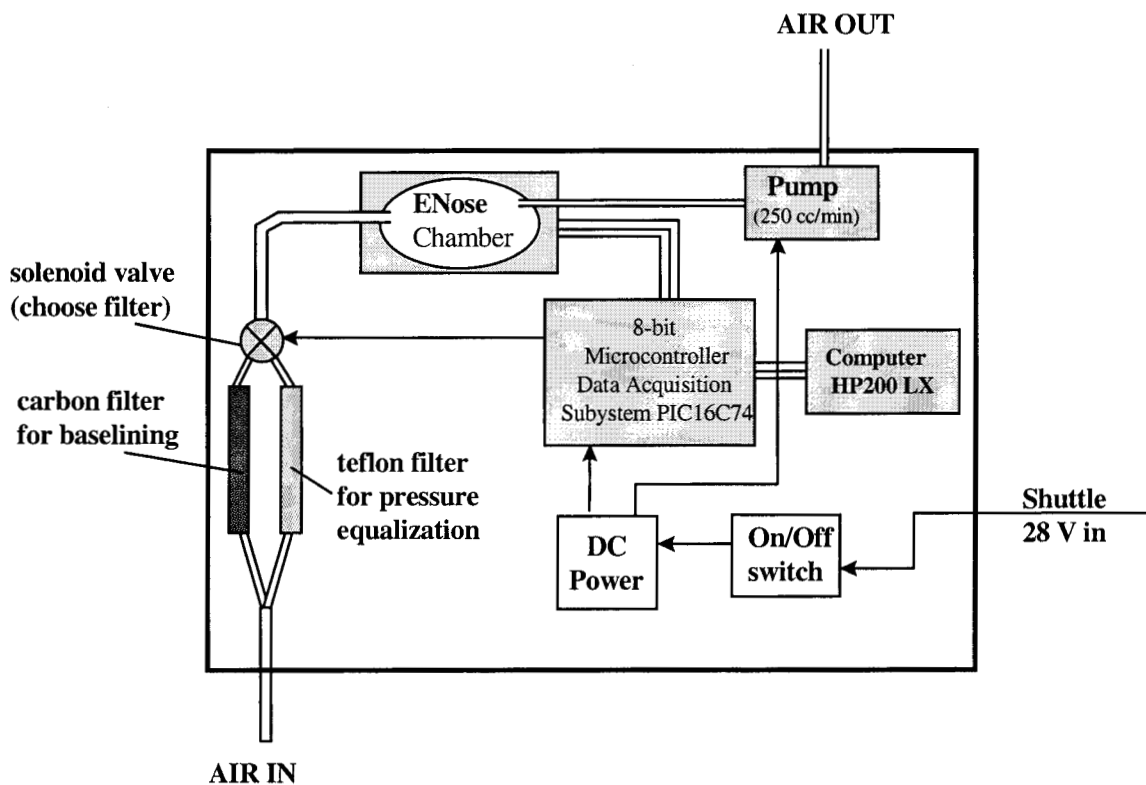
Figure 7.1 Diagram of JPL ENose flight unit.

Volume:	1700 cm^3
Mass:	1.4 kg
Power:	1.5 W average, 3 W peak

10 cm
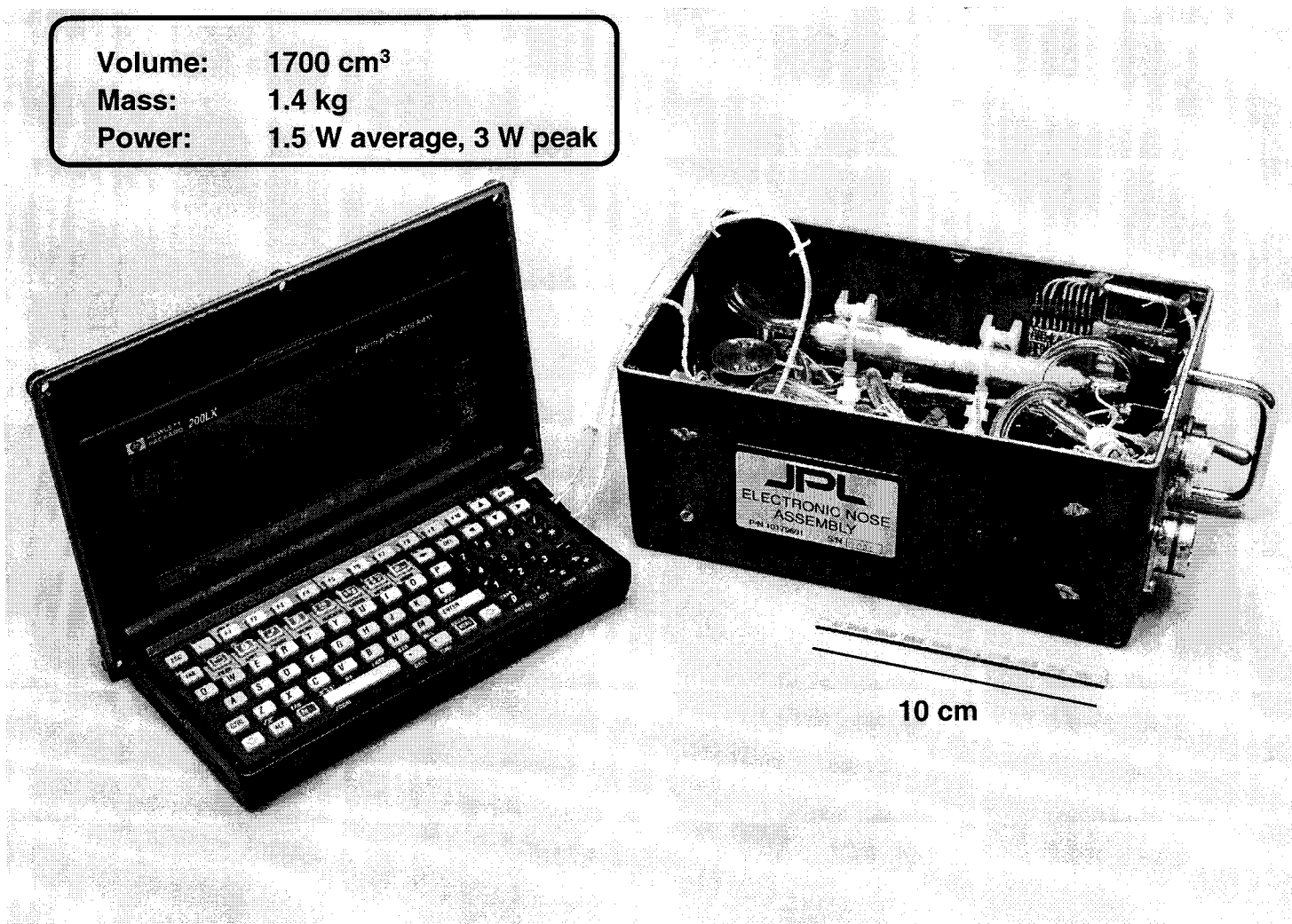
Figure 7.2 *ENose Assembly with the HP200LX Computer. The computer is held to the inside of the lid with velco, and the entire assembly was deployed in the middeck on STS-95 (see Figure 7.4).*
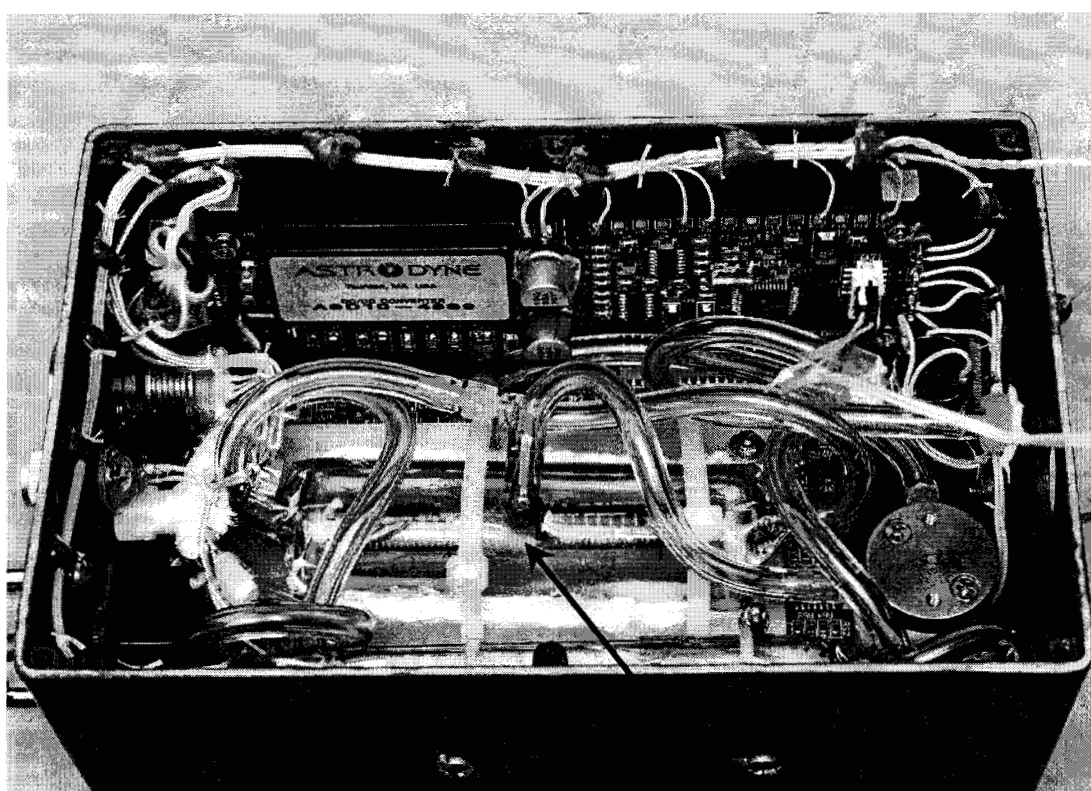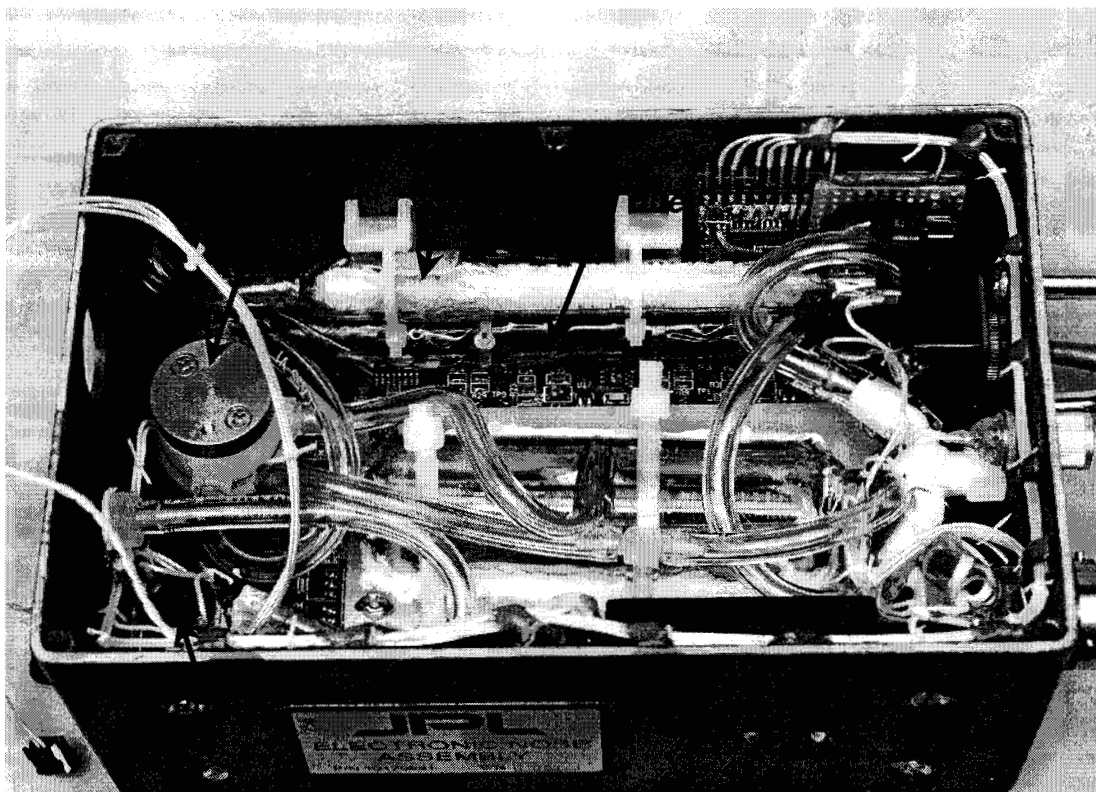
our sensor chips
Figure 7.3 Interior views of the ENose without the HP200LX Computer

Figure 7.4 ENose in place in middeck during STS-95. ENose is located near an air intake vent and is above Col. Glenn's left ear.

7.1 Mechanical Design

The mechanical design of the flight unit began with identifying a flight-qualifiable container. On the advice of JSC Shuttle Integration engineers, a cast aluminum container was selected and anodized. After identification of the components that would be included in the flight unit, a design for assembly was made. The mechanical design was reviewed by the JPL SAMRC committee and approved.

7.2 Pneumatic Design

The first part of the flight unit to be defined was the pneumatic system. It was determined early on in the program that it would be necessary to use a miniature pump to pull air through the sensor chamber in the flight unit in order to make measurements on the constituents in the air. Leaving the sensors in still air would result in very slow responses in the sensors, and possibly excessively slow sensor recovery from an event. Consultation with fluid mechanicians led to the selection of a diaphragm (pulsed) pump, in order to ensure turbulent flow in the sensing chamber. Laminar flow could result in partitioning of contaminants in the sensing chamber, and thus would result in irreproducible responses. The pump was put behind the chamber so that air was pulled over the sensors, and any dead space in the pump where contaminants could be trapped would not result in contamination later in the experiment. The sensor chamber was designed accordingly and was minimized to ~15 cm^3 in volume. The pump selected is a Thomas model X-400 miniature diaphragm pump, which flows air at 0.25 liters/minute.

Laboratory testing and the Early Human Test Chamber Experiment showed the utility of including a reference or baselining cycle in the data acquisition routine. The reference cycle is used to construct the baseline to correct for low frequency drift, and to determine whether there has been slow buildup of contaminants.

In the reference cycle, an activated charcoal filter is used to trap species in the air which would not generally be found in clean air. At intervals programmed into the control computer, a solenoid valve turns on and directs the intake air through the charcoal filter. When the valve is off, intake air is directed through a dummy filter. When clean air is directed through the charcoal filter the sensors' response is no different from the response with the dummy filter. The dummy filter is made of an inert material such as glass or Teflon beads to provide a similar pressure drop under filtered or unfiltered conditions. Compounds on the target list are reasonably well collected by the charcoal filter and water is passed by the filter, so there is no humidity change associated with the reference cycle. Formaldehyde is only partially collected, but a sufficient quantity is collected to provide baselining information. The length and width of the charcoal filter was determined by calculating equivalent plates and assuming collection of SMAC levels of all target compounds for 1 hour of operation.

In the flight unit, the filtering scheme to allow for baselining was altered slightly from the scheme used in the EHTC model. Activated charcoal was used as the filtering material, and Teflon® beads were used as the dummy filter provided to match the pressure change induced by the charcoal filter. A three-way solenoid valve with a Teflon® interior

was placed after the two filters to select the flow route. The reference cycle time used in the flight experiment was 15 minutes of filtering after 3hours of data.

The sensor chamber in the flight unit was a 15 cm^3 glass dome through which the pumped air was passed. The sensor chips were inserted into receptacles and the glass dome placed over them. The receptacles and dome were sealed to a copper-coated platform using electronic grade RTV$^®$ silicon rubber glue. All the parts of the system were connected using Tygon$^®$ tubing; where necessary polypropylene connectors were used. All connections were sealed with RTV$^®$.

When the problem of Tygon$^®$ tubing was identified in the laboratory gas handling system, the flight unit had already been delivered to JSC. Changing that tubing for Teflon$^®$ would have required a new mechanical design for the unit. Because the Tygon$^®$ tubing did not develop problems with gas retention until it had been operated with relatively high concentrations of the target compounds for several months, it was determined the tubing would not pose a problem for the short, 6-7 day period of operation of the ENose flight unit. After the unit was returned from the flight, it was tested with the hydrocarbon analyzer to determine that the delivered concentration of methanol was expelled from the pump. The air/methanol mixture that was collected after the pump in the flight unit had a methanol concentration within 5% of the delivered concentration.

7.3 Electronics Fabrication for Data Acquisition and Electronic Control
The unit was built using commercially available, mostly surface mount, components assembled on standard 4-layer FR4 printed wiring boards. The four sensor alumina substrates accommodated the polymers on one side and a unique resistor pattern on the back. These resistors were used to heat the substrates. Electrical connection to the substrates was through a small edge connector. Substrate temperature was controlled by a JPL developed closed loop control with the computer in the loop. While there are no new circuits in the ENose, the fusion of control and measurement circuits with the HP200LX is novel.

7.3.1 HP200LX Control The HP200LX computer was attached inside the ENose to the top of the ENose aluminum container by Velcro$^®$ strips. For flight the computer top was closed and secured by a tie-wrap The HP200LX controls the timing of the experimental measurements and archives the data. It also performs the display function and converts the voltages read at constant current to resistance. The archived data are stored in raw format as this preserves the most information and is dense. The program is written in QuickBasic 4.5, uses National Instrument "Lab Windows" driver calls and Microsoft C5.1; all compiled and linked to create an executable file. As shown in Fig. 7.1, the computer communicates directly with, and commands, a local microcontroller, a PIC16C74. (See 7.3.3 below).

7.3.2 Circuit Boards The ENose device includes two circuit boards: an analog board and the microcontroller digital board. The analog board has 4 identical channels of sensor measurement circuitry, and analog temperature control feedback loops for each

substrate, or sensor chip. Providing four channels makes it possible to take measurements several times a second, if necessary. Each analog channel has one ADC and two DACs, these are each 12 bit. The temperature controller has one 4 channel 8 bit DAC. The sockets for the sensor chips are mounted directly to the analog board (see section 7.1).

For the flight unit, the circuit shown in Firgure 4.2 was modified to enable the electronics to be run from a single 0-5 volt supply (see Figure 7.2). This is essentially the same circuit with the ground on the DAC $V1_i$ floating. The sensor resistance is determined by equation:

$$R_{SENi} = [(Vout + V2_i)/(1 + (R2/R1)) + V2_i) - V2_i]/(V1_i/Ro)$$

The digital board controls each individual measurement as well as the temperature control, pump and valve. This board also has the switching power converter that isolates the circuitry from the power lines and allows the ENose to run from a wide range of voltages.
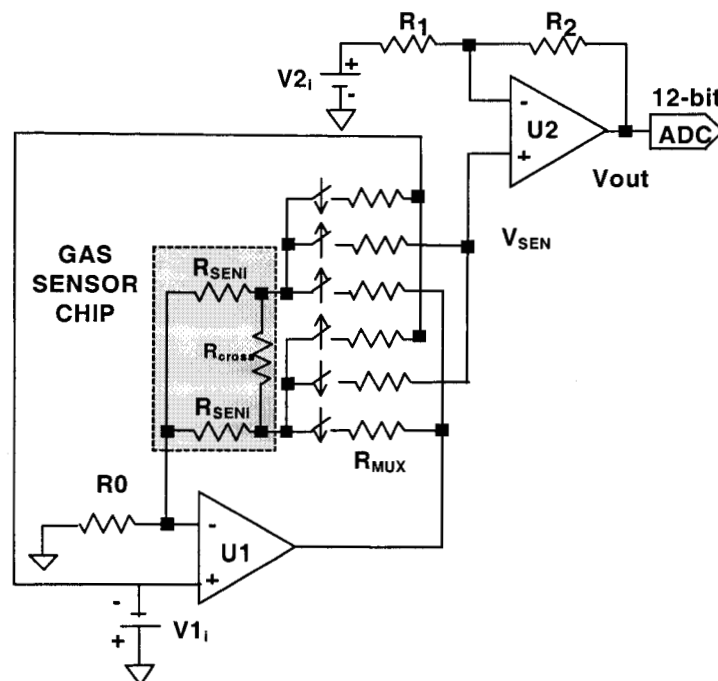
Figure 7.2 *Flight Unit Data Acquisition Circuit: 12 Bit Dual Offset Nulling Amplifier*

7.3.3 Microcontroller The PIC16C74 microcontroller is programmed in assembly language to command all the ENose components. It controls the reading and writing to the DACs and ADCs, the storing of measurement parameters for the 32 sensors to quickly multiplex between sensors, the switching of the pump and valve (under HP

command), the monitoring of temperatures and voltage, reading and setting of the real time clock, and initial boot and HP200LX power on and boot.

7.4 Flight Unit Assembly
The flight unit was assembled at JPL. The electronic components and electrical wiring as well as pneumatic components which needed power (valve, pump) were installed by the Electronic Packaging and Fabrication Section at JPL in their flight certified facility. The tubing and sealing were done in the Electronic Nose Lab in a clean bench.

8. STS-95 FLIGHT EXPERIMENT RESULTS

The ENose is designed to monitor for common contaminants in space shuttle air. To test the device's ability to detect target contaminants, an in-flight experiment was conducted on STS-95. After the device was removed from storage and turned on, it took data automatically and autonomously for 6 days. To verify that the device was operating as tested on the ground and to confirm the timekeeping, an alcohol wipe made of 70% 2-propanol, balance unknown, was used to create a daily event which was used as a daily marker. Before creating the event, a daily air sample was collected in a Grab Sample Container (GSC) provided by JSC for later independent GC-MS analysis.

Initial, visual examination of the flight data received indicates that the ENose responded to all planned wipe events, and that the responses were timely and distinguishable. Software event identification and data analysis further confirmed all planned wipe events. In addition to the wipe events, the device responded to a number of other events. Software analysis identified all events which were not wipe events as humidity changes. Many of those changes can be correlated in time with the humidity changes recorded by the independent humidity measurements provided to JPL by JSC. Those events identified as humidity changes but not correlated with cabin humidity change are likely to be caused by local humidity changes; that is, changes in humidity near the ENose which were not sufficient to cause a measurable change in cabin humidity. The independent humidity monitor was located in the stairway between the middeck and the flight deck, and so would not record any humidity changes localized around the ENose. Figures 8.1 a&b show how cabin humidity correlates with ENose response in several cases.

Figure 8.2 shows the similarity between the pattern for particular events in Figure 8.1, and compares them with the patterns recorded in training sets for exposure to the wipe and for humidity change. Software analysis of the flight data did not identify any other target compounds, as single gases or as mixtures. The results of the software analysis of the 46 peaks identified as events are presented in Appendix D. The analysis program returned an identification and quantification of each wipe event, and every other event was identified and quantified as a change in humidity.

The independent GSC analysis provided by JSC confirmed that no target compounds were found in the daily air samples in concentrations above the ENose detection threshold. Copies of the GC-MS analysis report are included in this report as Appendix E.

The correlation between the ground training and in-flight response patterns for both the alcohol wipe and humidity change shows that the operation of the ENose is microgravity insensitive, and thus can be used in a space-based application without further accounting for microgravity effects.
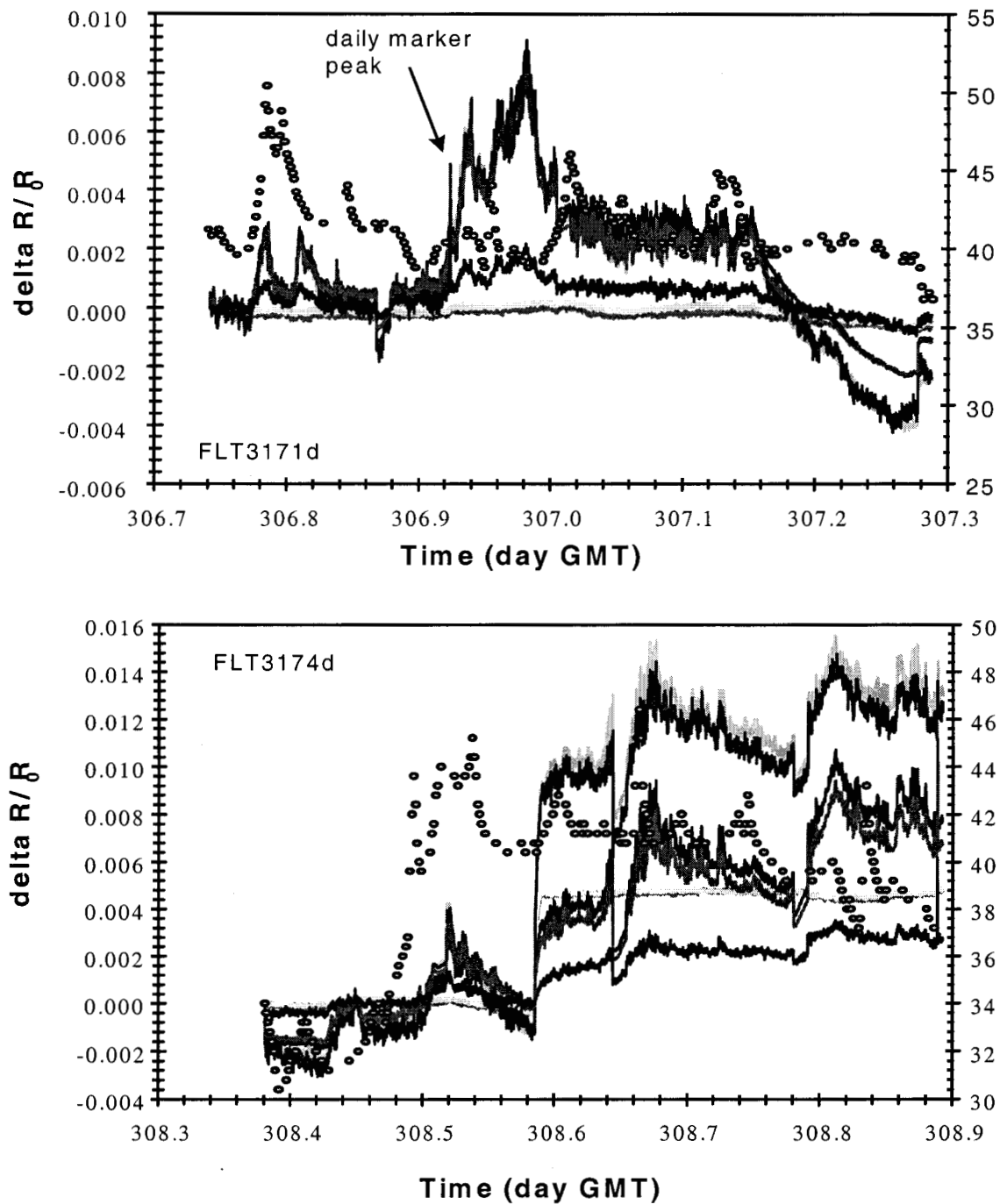
Figure 8.1 *a,b) STS-95 Shuttle Data. Circles are the plot of independent humidity measurements in the stairway from mid-deck to flight deck and colored lines plot the response of different sensors in the ENose, Note that at times when there is a major excursion in cabin humidity, the ENose responds, as well. The step at time 308.58 is a temperature change; cabin temperature approached the ENose chip set point, so the ENose temperature was raised 4°C. The daily marker in FLT3174d occurs at the end of the plot, at time 308.89.*
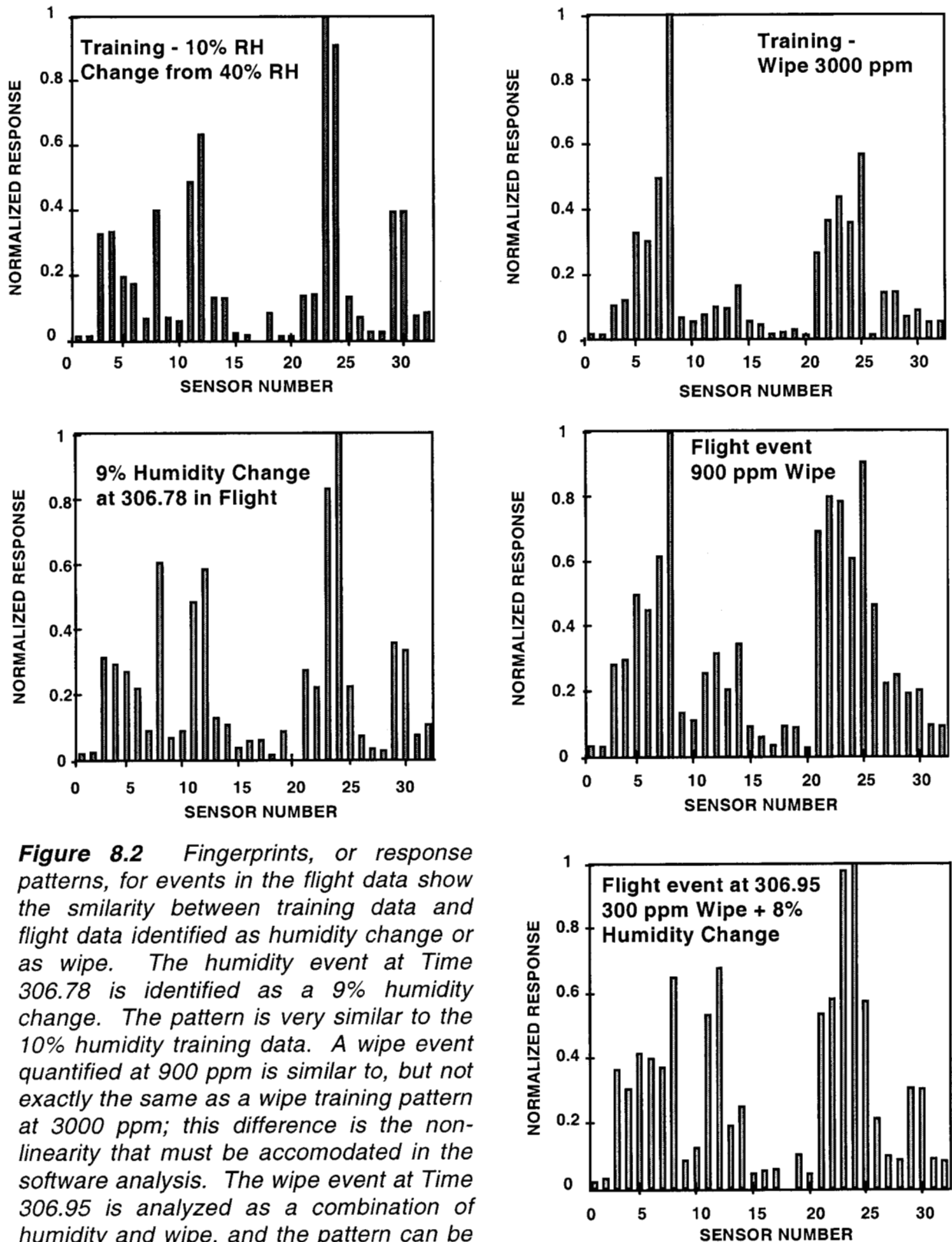
Figure 8.2 *Fingerprints, or response patterns, for events in the flight data show the smilarity between training data and flight data identified as humidity change or as wipe. The humidity event at Time 306.78 is identified as a 9% humidity change. The pattern is very similar to the 10% humidity training data. A wipe event quantified at 900 ppm is similar to, but not exactly the same as a wipe training pattern at 3000 ppm; this difference is the non-linearity that must be accomodated in the software analysis. The wipe event at Time 306.95 is analyzed as a combination of humidity and wipe, and the pattern can be seen to be a combination of the two training patterns.*

9. SUCCESS CRITERIA FOR ELECTRONIC NOSE TESTING

Success criteria for ground testing and for flight were set with the agreement of the co-investigator, Dr. John James of JSC. Three of four success criteria for ground testing were met before flight; criterion #3 was met partially. All success criteria for flight were met within the limit of the events of the flight (*e.g.* criterion #6 could not be met because there were no events which were unknown.) The success criteria and how they were met are discussed below.

9.1 Success Criteria For Ground Testing

1. *Target compounds can be detected, identified and quantified at +/- 50% the one-hour SMAC level or lower by applying the analysis software developed for the purpose.*

Nine of ten compounds on the target list can be detected, identified, and quantified at or below the SMAC level. Formaldehyde can be detected, identified and quantified at 15 ppm (SMAC is 0.4 ppm). Identification accuracy overall is ~ 90%.

2. *Mixtures of 2 & 3 targeted gases can be detected, identified and quantified at +/- 50% the one-hour SMAC level or lower by applying the analysis software.*

Exhaustive mixture testing was not undertaken. Several mixtures containing propanol, ethanol, ammonia, formaldehyde. toluene and benzene have been tested, and the constituents detected, identified and quantified as required.

3. *Contaminants in a pre-mixed sample of 4 gases can be identified and quantified at +/- 50% the one-hour SMAC level or lower by applying the analysis software.*

Data were recorded for analysis, but because the software analysis routines did not have a significant level of success on mixtures greater than three, they were not analyzed. Mixtures of two and in some cases three gases were successfully analyzed, but those data were not taken from pre-mixed samples

4. *ENose data analysis segregates compounds which are not on the target list.*

Analysis of single and multiple gases successfully segregates unknowns, >90%.

9.2 Success Criteria For Shuttle Flight Experiment

1. *Successful delivery and acceptance to flight.*

Delivered to JSC May 19, 1998.

2. *Device operates continuously (while turned on) as programmed, and data are retrieved after flight.*

Operated continuously for 6 days during flight with no problems. Data were retrieved with no corrupted files.

3. *Sensor responses correlate with the shuttle logged events of sufficient concentration*

No shuttle logged events for correlation. Responses do correlate to rises and falls in cabin humidity as recorded by independent humidity monitor.

4. Data analysis software correctly identifies and quantifies planned events .

All planned events (daily marker of propanol wipe) were correctly identified. Marker events were quantified in the 500-1000 ppm range, which is within range found for similar tests done in the laboratory.

5. Data analysis software correctly identifies targeted compounds at or above the one-hour SMAC level and quantifies them at +/-50%, confirmed by the GC-MS analysis of the Grab Sample Container contents.

There were no compounds on the target list found at the one-hour (or even 24-hour) SMAC level during the time the ENose was running. The ENose did not record false positives.

6. Data analysis software classifies as "unknown" compounds which are detected and are not on the target list.

There were no false positive events; neither were there events during the flight which could not be identified. All events which were not 2-propanol daily marker events were identified as humidity changes.

10. CONCLUSIONS AND PLANS FOR FURTHER WORK

In January, 1999 John James, Tom Limero and Helen Lane of JSC, and M. A. Ryan, Margie Homer, Darrell Jan and Hanying Zhou of JPL met to review the ENose flight data and the independent ground analysis (GC-MS) of the air samples taken during flight. In that meeting, several conclusions regarding the flight experiment were discussed. The participants agreed that the ENose Flight Experiment was a successful one. The approach to using insulating polymers loaded with a conductive medium which was developed at Caltech was taken from a laboratory demonstration to development of a miniature demonstration device which operated continuously in a microgravity environment. The demonstration was successful in that all events recorded were analyzed by the software, and in many cases could be correlated to independent measure of cabin events. The primary conclusions reached in that meeting were that the ENose operated without incident, that all planned events (daily markers) were detected and that there were no inconsistencies between the data analysis from the ENose and from the GC-MS within detection limits of the techniques.

While the hope in an experiment such as this one is that there will be several events which test the ability of the device, such events would certainly be anomalous events in the space shuttle environment. The fact that the shuttle air is largely uneventful and clean is, of course, desirable for the crew, but made for an uneventful experiment and did not significantly challenge either the response characteristics or the software analysis routines of the ENose. It is not surprising that the only unplanned events

recorded by the ENose were humidity changes, and it is because events were not expected that the experiment included the relatively uncontrolled daily marker events. Locating the ENose near the intake for the air revitalization system was a good choice of location, and unremarkable events (such as use a crew member passing by or using a product such as deodorant) were not recorded. Also, metabolic products such as methane below 3000 ppm and hydrogen did not result in responses in the sensors. Localized events were sufficiently diluted as not to cause response in the ENose sensors. There were no events reported by the crew that would be expected to induce a response in the ENose. However, further work on the ENose, especially if the plan is to use many small, distributed sensor heads, will have to take localized events into account.

For the two compounds seen, water in quantities sufficient to constitute a change in relative humidity (a humidity change from 35-40% at 30°C is approximately 3000 ppm), and the alcohol wipe, the response of the ENose in microgravity was not significantly different from the response on the ground. This result leads to the conclusion that the device is microgravity insensitive.

The shuttle air was warmer than was expected from the EHTC experiment, and so the ability of the on-chip heaters was challenged. They performed well and kept the temperature of the chips steady, but if the air had been warmer than it was, generally around 30°C, the chip heaters would have been insufficient. The next generation ENose will take the temperature into account. It has been found in ground testing that heating the chips rather than the air can lead to excessive noise in the response; further investigation of heating the chamber or eliminating the need to heat altogether will be planned for the next phase.

For the flight experiment, the size charcoal filter used was calculated to fit the experiment. Using PTFE beads in the dummy filter in the flight experiment was not as effective as using glass beads in the dummy filter in the EHTC experiment. The need for filtering for baseline control will need to be further considered.

The events seen, wipe in particular, but in some cases humidity change, were shorter than the training events. The noise filtering used in the software then could lead to obscuring some events. Thus, future work will use shorter training events.

The limitations of the flight experiment were primarily in the lack of events for analysis. As it is unlikely that it will be possible to stage a number of different events during a flight to challenge the abilities of the ENose, the group that met in January, 1999 concluded that in the absence of such a flight experiment, resources would be better applied to extensive ground testing, including blind testing of the software analysis in a relevant environment as well as inclusion of the ENose in future module tests such as Bioplex. The group also agreed that the best application of the ENose for Space Station use would be twofold: as an incident monitor to warn crew members of anomalous events such as leaks, spills, air filter breakthrough and incipient fires; and to monitor the progress of clean-up activities after an anomalous event. The relatively

wide dynamic range accessible to the ENose makes it an excellent device for application to these uses. It does not, and probably will not, have the capability to be used as an analytical instrument or to analyzed all the constituents in a vapor sample, but can be used in concentration regimes where a GC-MS cannot.

Further work with the ENose should take account of the limitations of the experiment done in this program. While the experiment was controlled to the extent that daily air samples were taken and daily confirmation of the device's operation was made, it was not controlled in that an event which occurred several hours away from the time of sampling would not be picked up by the sample. Truly testing the ENose as an incident monitor will require controlled release of target compounds, mixtures of target compounds, and unknowns. This scenario is not a likely one for use in a flight environment, as it will pose risk to crew health.

A proposal for further work to follow this final report will propose a program in which the ENose developed in this program will be further developed and tested extensively on the ground, with the goal of producing an incident monitor, with a detection range from single ppm to hundreds of ppm. The major points of this proposal will include:

1. The device will be further miniaturized
2. The list of target compounds will be expanded in consultation with JSC.
3. The number of polymers will be expanded to 32.
4. The target concentrations for contaminants will be pushed to the 24-hour SMAC.
5. Extensive ground testing with controlled release of contaminants in an environment similar to that of the space shuttle will be undertaken.
6. Data analysis software will include the capability for real-time analysis.

11. REFERENCES

1. M.S. Freund and N.S. Lewis, "A Chemically Diverse Conducting Polymer-Based Electronic Nose," *Proc. Natl. Acad. Sci.*, **92**, 2652 (1995).

2. M.C. Lonergan, E.J. Severin, B.J. Doleman, S.A. Beaber, R.H. Grubbs, and N.S. Lewis, "Array-Based Vapor Sensing Using Chemically Sensitive, Carbon Black-Polymer Resistors," *Chem. Materials*, **8**, 2298 (1996).

3. B.J. Doleman, R.D. Sanner, E.J. Severin, R.H. Grubbs, and N.S. Lewis, "Use Of Compatible Polymer Blends To Fabricate Arrays Of Carbon Black-Polymer Composite Vapor Detectors," *Anal. Chem.,* **70,** 2560 (1998).

4. H.V. Shurmer and J.W. Gardner, "Odour Discrimination with an Electronic Nose," *Sensors and Actuators*, **B8**, 8, (1992).

5. J.W. Gardner, T.C. Pearce, S. Friel, P.N. Bartlett and N. Blair, "A Multisensor System for Beer Flavour Monitoring Using and Array of Conducting Polymers and Predictive Classifiers," *Sensors and Actuators*, **B18-19**, 240, (1994).

6. J.T. James, *et al.*, *Aviation, Space Environ. Med.*, **65**, 851 (1994).

7. *Spacecraft Maximum Allowable Concentrations for Selected Airborne Contaminants*, Vols. 1 & 2, National Academy Press, Washington, DC (1994).

8. *Space Physiology and Medicine*, A.E. Nicagossian, C.L. Hunton & S.L. Pool, eds., Lea and Febiger, Philadelphia (1994).

12. PAPERS AND PRESENTATIONS

"Results From The Space Shuttle STS-95 Electronic Nose Experiment*"*
M. A. Ryan, M .G. Buehler, M .L. Homer, K. S. Mannatt, B. Lau, S. Jackson, and H. Zhou, *Proceedings of the Micro/NanoTechnology 99 Conference*, Pasadena CA (1999).

"Monitoring Space Shuttle Air for Selected Contaminants Using an Electronic Nose, " M. G. Buehler, M. A. Ryan, M. L. Homer, K. S. Manatt, B. Lau, S. Jackson, and H. Zhou, 5th International Symposium on Olfaction and Electronic Noses (Baltimore, MD), September 1998.

"Monitoring Space Shuttle Air for Selected Contaminants Using an Electronic Nose"
M. A. Ryan, M. L. Homer, M. G. Buehler, K. S. Manatt, F. Zee, B. Lau, D. Karmon, V. Ryan, A. Kisor, S. Jackson, *Proceedings of the 28th International Conference on Environmental Systems* (1998).

"Development and Testing an Electronic Nose at JPL"
M. L. Homer, M. A. Ryan, M. G. Buehler, K. S. Manatt, S. Jackson and A. Kisor, NASA Workshop on Advanced Environmental Monitoring, October 1997.

"Test Structures Applied to the Rapid Prototyping of Sensors"
M. G. Buehler, L.-J. Cheng, and D. P. Martin, *Proceedings of the IEEE International Conference on Microelectronic Test Structures*, **10**, 212-218, March 1997.

"Temperature and Humidity Dependence of a Polymer-Based Gas Sensor"
M. G. Buehler and M. A. Ryan, SPIE Conference on Electro-Optical Technology for Chemical Detection and Identification, 21 April 1997.

"Monitoring the Air Quality in a Closed Chamber Using an Electronic Nose"
M. A. Ryan, M. L. Homer, M. G. Buehler, K. S. Manatt, F. Zee, J. Graf, *Proceedings of the 27th International Conference on Environmental Systems* (1997).

"Electronic Nose Technology at JPL"
M. A. Ryan, M. G. Buehler, K. S. Manatt, V. Shields, L.-J. Cheng, D. Karmon, F. Zee; NASA Workshop on Advanced Environmental Monitoring, September 1996.

13. TECHNICAL STAFF

The ENose project was divided into five main tasks, as described above. The Principal Investigator for the project was Dr. Margaret A. Ryan. The Task Manager for the project was Dr. Dan Karmon.

Several technical staff members were involved in more than one task, but are listed here in their primary capacity. This is not an exhaustive list of staff involved in this work, but lists those people who were responsible for major areas of work.

Sensor Development and Test
Margie L. Homer
Darrell L. Jan
Margaret A. Ryan

Coordination with JSC
Dan Karmon
Karan L'Heureux

Data Acquisition and Control
Martin G. Buehler
Kenneth S. Manatt

Flight Unit Design and Fabrication
Shannon Jackson
Roy Packard
Yuki Salinas

Data Analysis Software
Brian Lau
Frank Zee
Hanying Zhou

Undergraduate students who participated in this program
Roger H. Cortez, Occidental College
Adam K. Kisor, University of California at San Diego
Victoria Ryan, California State University at Long Beach

APPENDIX A: CONFERENCE PROCEEDINGS PAPER

"Monitoring Space Shuttle Air for Selected Contaminants Using an Electronic Nose," M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, B. Lau, D. Karmon and S. Jackson; presented at The 28th International Conference on Environmental Systems, Danvers MA, July 12-16, 1998.

981564

Monitoring Space Shuttle Air for Selected Contaminants Using an Electronic Nose

M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, B. Lau, D. Karmon and S. Jackson

Jet Propulsion Laboratory, California Institute of Technology
Pasadena CA 91109

ABSTRACT

A miniaturized electronic nose has been constructed at JPL in collaboration with Caltech. This array of conductometric sensors has been trained to detect and quantify the presence of vapors in the air; the compounds detected have been found as contaminants in shuttle air. This device has potential application as a miniature, distributed device for monitoring and controlling the constituents in air.

INTRODUCTION

The ability to monitor the constituents of the breathing air in a closed chamber in which air is recycled is important to NASA for use in closed environments such as the space shuttle and the space station. At present, air quality is determined after the fact by collecting samples and analyzing them on the ground in laboratory analytical instruments such as a gas chromatograph-mass spectrometer (GC-MS). The availability of a miniature, portable instrument capable of identifying contaminants in the breathing environment at part-per-million levels would greatly enhance the capability for monitoring the quality of recycled air as well as providing notification of the presence of potentially dangerous substances from spills and leaks. Such an instrument is the Electronic Nose now under development at JPL and Caltech [1-3].

An electronic nose is an array of non-specific chemical sensors, controlled and analyzed electronically, which mimics the action of the mammalian nose by recognizing patterns of response to vapors. The sensors used here are conductometric chemical sensors which change resistance when exposed to vapors. The sensors are not specific to any one vapor; it is in the use of an array of sensors, each with a different sensing medium, that gases and gas mixtures can be identified by the pattern of response of the array. Electronic Noses have been discussed by several authors, and may be applied to environmental monitoring and quality control in such wide fields as food processing, and industrial environmental monitoring [4,5].

A baseline of clean air is established, and deviations from that baseline are recorded as changes in resistance of the sensors. The pattern of distributed response of the sensors may be deconvoluted, and contaminants identified and quantified by using a software analysis program such as pattern recognition and/or neural network.

At present, the best real time, broad band air quality monitor available in space habitats is the human nose. It is limited by human factors such as fatigue and exposure to toxins. Most existing chemical sensors are designed to detect specific molecules. Array-based sensing uses non-specific sensors in which the pattern and magnitude of response are used to identify and quantify the presence of contaminants. Array-based sensors are based on a biological model of "sniffing", detecting changes in odor, and can be trained to detect new patterns.

The overall goal of the program at JPL/Caltech is the development of a miniature sensor which may be used to monitor the breathing air in the international space station, and which may be coordinated with the environmental control system to solve air quality problems without crew intervention. Progress toward that goal will depend on the success of this portion of the Electronic Nose program, which is the development of a prototype system which will be the subject of an experimental test during a space shuttle flight in 1998.

THE ELECTRONIC NOSE DEVELOPMENT MODEL

The conductometric sensors used in the Electronic Nose (ENose) built at JPL are polymer films deposited on gold contacts. The films are made from polymers in which a conductive medium, carbon black, has been dispersed [2].

Presence of a contaminant in air is measured as a change in resistance in the polymer films. Sensor response is expressed as a ratio of change in resistance at time t to resistance at time t=0, $(R_t-R_0)/R_0$. Data are acquired on a Hewlett Packard HP200 LX palm top

computer using a program written for this purpose in LabWindows.

DESIGN OF SENSOR HEAD

<u>Substrate and Sensing Films</u>   The sensor head of the Electronic Nose used in this experiment consists of 32 sensor positions arranged on 4 substrates, each with 8 sensor positions. The substrates were made using hybrid microelectronic cofired ceramic (alumina) processes.   Electrodes and contacts were deposited as thick films using screen printing. The substrate layout and fabrication has been discussed in detail elsewhere [9]. A guard ring is used around each sensor to minimize cross-talk and sensor interaction. A sketch of a sensor chip is shown in Figure 1.
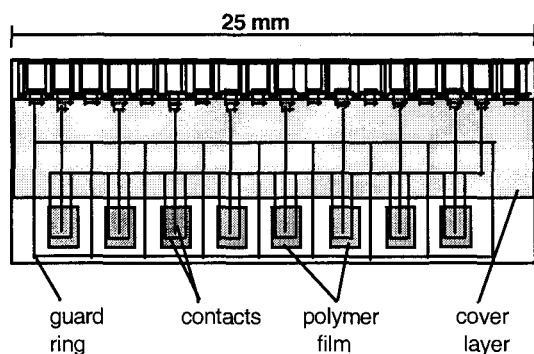
Figure 1: Sketch of the ceramic substrate chip containing eight sensors

The polymeric sensor films were made by depositing a solution of polymer mixed with carbon black to make a film 1 - 5 microns thick in contact with gold electrodes. 16 polymers were used in this experiment, four on each ceramic substrate. Each polymer was deposited in 2 positions on each chip, with the positions side-by-side to ensure that each sensor would see the same vapor environment. A thermistor is included on each chip and on the sensor head for temperature monitoring.

Temperature can be controlled from room temperature to 36°C using RuO2 heaters deposited on the back of each chip in the ceramic fabrication process. The sensor resistance is sensitive to changes in temperature, so the ENose is operated with the sensors held at a constant temperature of 28°C.

The 16 polymers used are:

1. poly(2, 4, 6-tribromostyrene)
2. poly(4-vinylphenol)
3. poly (ethylene oxide)
4. polyamide resin
5. cellulose triacetate
6. poly (2-hydroxyethyl methacrylate)
7. poly (caprolactone)

8. vinyl alcohol/ vinyl butyral copolymer
9. poly (α -methylstyrene)
10. poly (vinyl chloride-co-vinylacetate)
11. poly (vinyl acetate)
12. poly (N -vinylpyrrolidone)
13. styrene/isoprene, block copolymer
14. poly (vinyl stearate)
15. methyl vinyl ether/ maleic acid
16. hydroxypropyl methyl cellulose

These polymers were selected by statistical analysis of the responses of 100 polymers to the set of contaminants listed in Table 1. Data for the statistical analysis were provided by Caltech [11]. The analysis selected the set of polymers which would result in the maximum difference in patterns of response.

<u>Deposition of Films</u>   160 mg of each polymer was dissolved in 15 mL of organic solvent. Solvents used were tetrahydrofuran (THF), acetone, dichloro methane, toluene or a mixture of solvents. 40 mg of carbon black was added to the solution, and dispersed by sonication. 1 - 3 μL of solution was pipetted onto the sensor area and allowed to dry in flowing, clean dry air while the sensor chip was held at 28°C. The resistance of the resulting films was in the range 1 -50 kΩ. Solution was added in increments of 1 μL until the desired resistance was reached. The use of polymer films as sensing media in an electronic nose has been discussed in detail by several authors, including the Caltech group working with JPL on this project [1-5].

ENOSE SYSTEM

A diagram of the ENose system used in this experiment is shown in Figure 2.
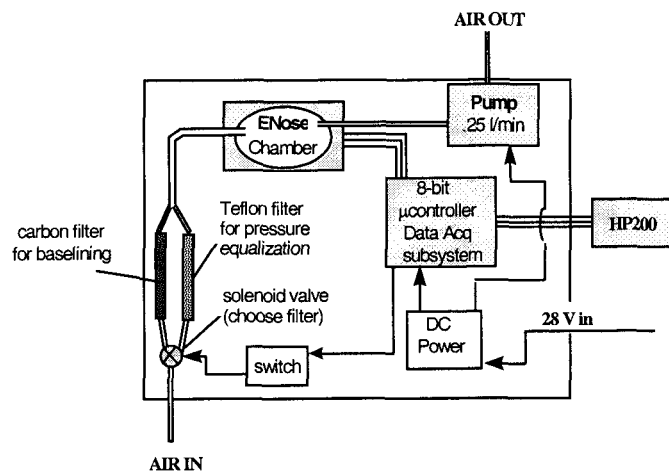
Figure 2: Diagram of ENose system.

Flowing air (.25 L/min) is pumped from the room into the sensor chamber of the ENose using a Thomas

model X-400 miniature diaphragm pump. The air is directed either through an activated charcoal filter, put in line to provide clean air baseline data, or though a dummy Teflon bead filter, put in line to provide a pressure drop similar to the charcoal filter. Solenoid valves are programmed to open the path to the charcoal filter and provide 30 minutes of clean air flow every four hours; otherwise, the air is directed through the Teflon bead filter. Air then enters the glass enclosed sensor head chamber where resistance is measured every 30 seconds, and then is returned to the room.

The experiment is controlled using a HP200 LX palm top computer and a circuit designed for the purpose [9,10]. The circuit is commanded by the HP 200 to operate the pump, to open and close the solenoid valve, and to acquire resistance data from the sensors by measuring the voltage at a current provided.
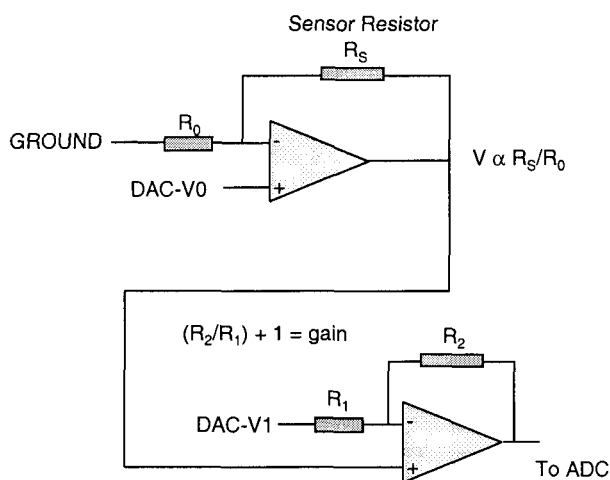

Figure 3: Diagram of ENose measuring circuit.

Data Acquisition and Control   Data acquisition and device control are accomplished using a PIC 16C74A microcontroller. The Hewlett Packard HP 200 LX palm top computer is programmed to direct the microcontroller to open or close the solenoid valve which controls access to the charcoal or Teflon filter and to record sensor resistance. Typical resistance change for 10-50 ppm of contaminant is on the order of 2×10^{-4} (200 ppm resistance change), and may be as small as $\times 10^{-5}$. The data acquisition circuit is shown schematically in Figure 3. Small changes in resistance are measured using a 12 bit dual offset nulling amp, in which a known current is put through the sensor resistor R_s by DAC-V0 and fixed resistor R_0. The voltage across the sensor is measured with precision by subtracting DAC-V1, an experimentally determined voltage, from V_s, the voltage drop across the sensor resistor, R_s. The difference is then multiplied by a fixed gain, $(R_2/R_1) + 1$, where R_2 and R_1 are fixed resistors. For each measurement, the DAC and ADC are locked to the same voltage reference, where DAC is Digital to Analog Converter (12 Bit

MAX538 and MAX539), and ADC is Analog to Digital Converter (12 Bit LTC1286).

Data are stored in flash memory in the HP 200, and are analyzed later using software designed for the task.

Data Analysis   The goal of the ENose development is the construction of an air quality monitor capable of identifying the target compounds in Table 1 at less than SMAC levels. To accomplish this goal, we have developed data analysis software which recognizes the patterns of response of the target compounds. The data analysis software forms, from training data, a characteristic vector of sensor responses for each target compound. The characteristic vector for an unknown compound is expressed as a linear combination of the characteristic vectors of the target compounds via a least squares solution using pseudo inverses computed by the singular value decomposition algorithm. The result is a listing of what quantities of which target compounds compose the unknown compound. At present, unknown compounds are expressed as a combination of up to four contaminants. In the case of exposure to a single contaminant, additional verification of the analysis is obtained by a standard backpropagation-trained neural network and by linear discriminant functions.

Table 1 shows the minimum concentration detected for each of the target compounds using the software analysis program, and Figures 4 a-d show the linear region of concentration detection. The goal of this program was to quantify contaminants +/- 50% of delivered concentration; the shaded region in the plots describes the 50% error region. Humidity was controlled from 20 -60 % relative humidity during training. Water content of the air raises the resistance of the sensors, and can either be deconvoluted from the response as a separate vapor, or zeroed out of the measurement if humidity has not changed since the last baseline.

CONCLUSIONS

The miniaturized ENose designed and built at JPL has the capacity to detect a limited suite of contaminants at 1 hour SMAC levels with +/- 50% accuracy. Combinations of four or fewer vapors can also be detected and deconvoluted for identification and quantification. The ENose experiment will be performed on a shuttle flight in 1998 to verify its operation. The experiment will consist of several steps:

a. ENose response will be recorded over 5 - 8 days

b. Daily calibration of ENose to 2-propanol done by a crew member

c. Daily air samples ("grab samples") taken for post flight analysis at JSC

Compound	Detected on shuttle (ppm) [6]	SMAC (ppm) [7,8] 1hr	Detected at JPL (ppm)
alcohols			
methanol	< 1	30	25
ethanol	.5 - 5	2000	50
2-propanol	.4 - 4	400	50
methane	1 - 1	5300	3000
ammonia	0	30	20
benzene	< .1	10	10
formaldehyde	0	0.4	10
Freon 113	.1 - 1	50	50
indole	0	< 1	0.03
toluene	.4 - 4	16	15

Table I: Compounds detected by the ENose, Spacecraft Maximum Allowable Concentration of each compound , and minimum concentration detected by this model ENose.

d.   Post flight analysis of data using software developed under this program

e. Post flight analysis of grab samples by gas chromatography/mass spectrometry

f.   Post flight comparison of analyzed ENose response to ground analysis of grab samples.

At its present level of maturity, the ENose is not an analytical instrument, but can be used to monitor an environment against a baseline, which is determined at intervals using filtered air.

Long-duration space flight requires a high level of crew productivity in tasks other than habitat maintenance. Decentralization of habitat control and de-coupling of spacecraft from ground control requires a move to a distributed network of small sensors and actuators. The ENose can be programmed to monitor habitat air for the presence of contaminants which exceed the Spacecraft Maximum Allowable Concentration (SMAC) and to sound an alarm or actuate remedial action, a form of feedback control. ENose sensors lend themselves to distribution of several miniature arrays linked to a common computer for control and analysis. The presence of several arrays distributed about the habitat will allow early identification of areas requiring remediation

REFERENCES

1. M.S. Freund and N.S. Lewis, *Proc. National Academy of Science*, **92**, 2652, (1995).

2. M.C. Lonergan, E.J. Severin, B.J. Doleman, S.A. Beaber, R.H. Grubbs and N.S. Lewis, *Chem. Materials,* **8**, 2298 (1996).

3. M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, F. Zee, and J. Graf, *Proceedings of the International Conference on Environmental Systems*, Society of Automotive Engineers, (1997).

4. H.V. Shurmer and J.W. Gardner, *Sensors and Actuators*, **B8**, 8, (1992).

5. J.W. Gardner, T.C. Pearce, S. Friel, P.N. Bartlett and N. Blair, *Sensors and Actuators*, **B18-19**, 240, (1994).

6. J.T. James, *et al.*, *Aviation, Space Environ. Med.*, **65**, 851 (1994).

7. *Spacecraft Maximum Allowable Concentrations for Selected Airborne Contaminants*, Vols. 1 & 2, National Academy Press, Washington, DC (1994).

8. *Space Physiology and Medicine*, A.E. Nicagossian, C.L. Hunton & S.L. Pool, eds., Lea and Febiger, Philadelphia (1994).

9. M.G. Buehler and M.A. Ryan, *Proc. Int'l Conf. on Microelectronic Test Structures* (March 1996).

10. M.G. Buehler and M.A. Ryan. *Proc. SPIE Conf. on Electro-Optical Tech. for Chemical Detection*, (April, 1997).

11. N.S. Lewis, California Institute of Technology, private communication.
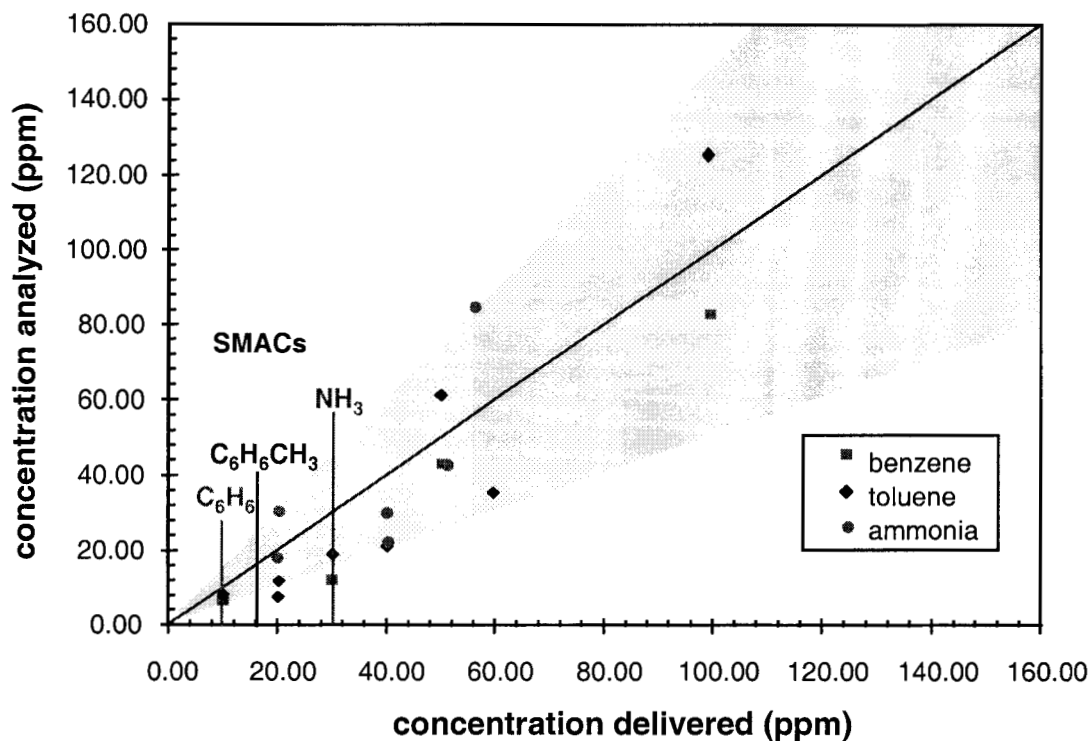
Figure 4a: Identification and Quantification of Benzene, Toluene and Ammonia. SMACs for each compound are marked on the plot. The shaded area is the +/- 50% target zone.
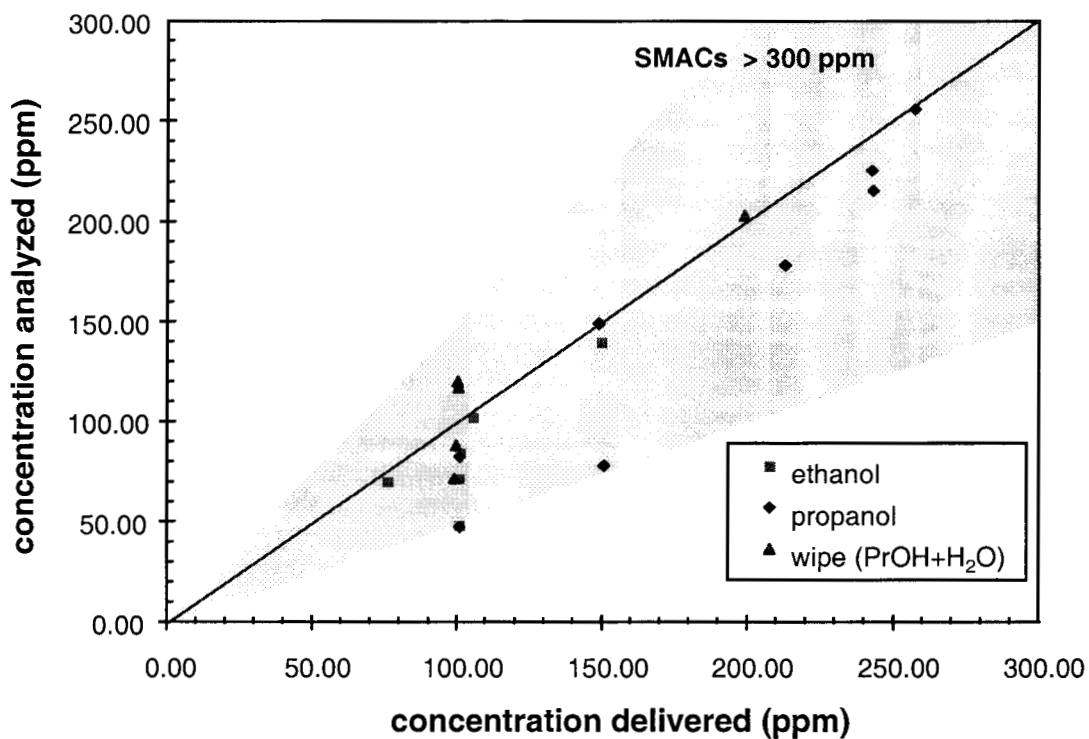
Figure 4b: Identification and Quantification of Ethanol, Propanol and the Propanol Wipe to be used as calibration. SMACs for each compound are marked on the plot. The shaded area is the +/- 50% target zone.
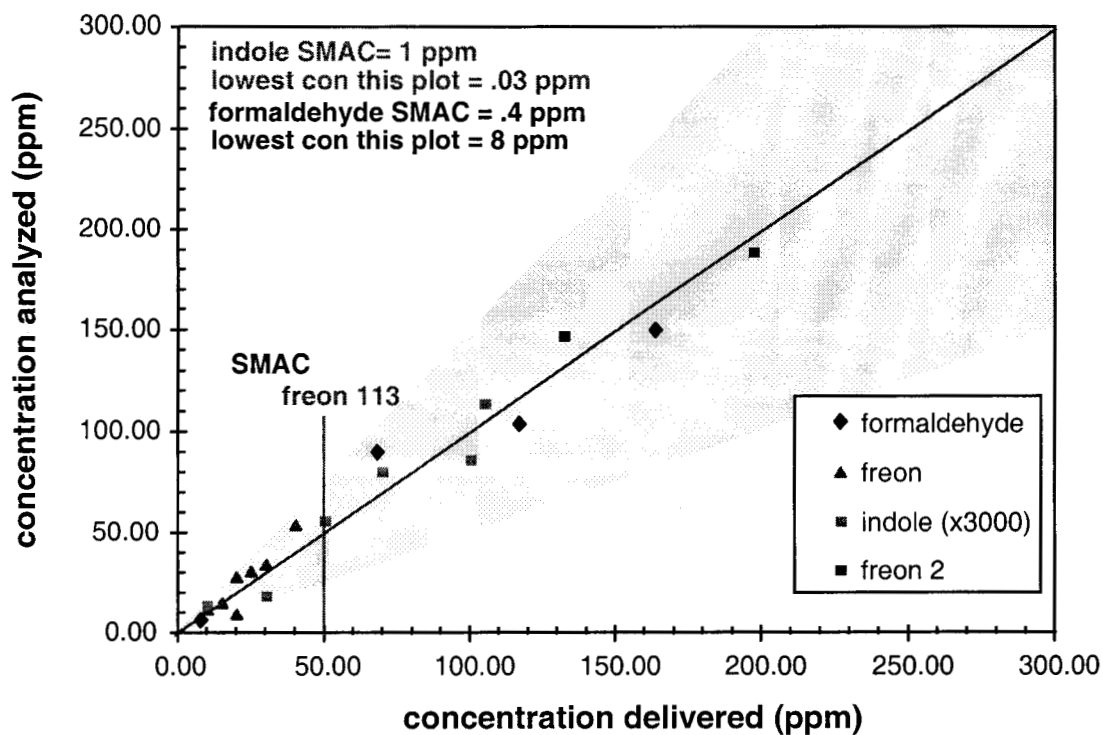
Figure 4c: Identification and Quantification of Indole, Freon 113 and Formaldehyde. SMACs for each compound are marked on the plot. The shaded area is the +/- 50% target zone.
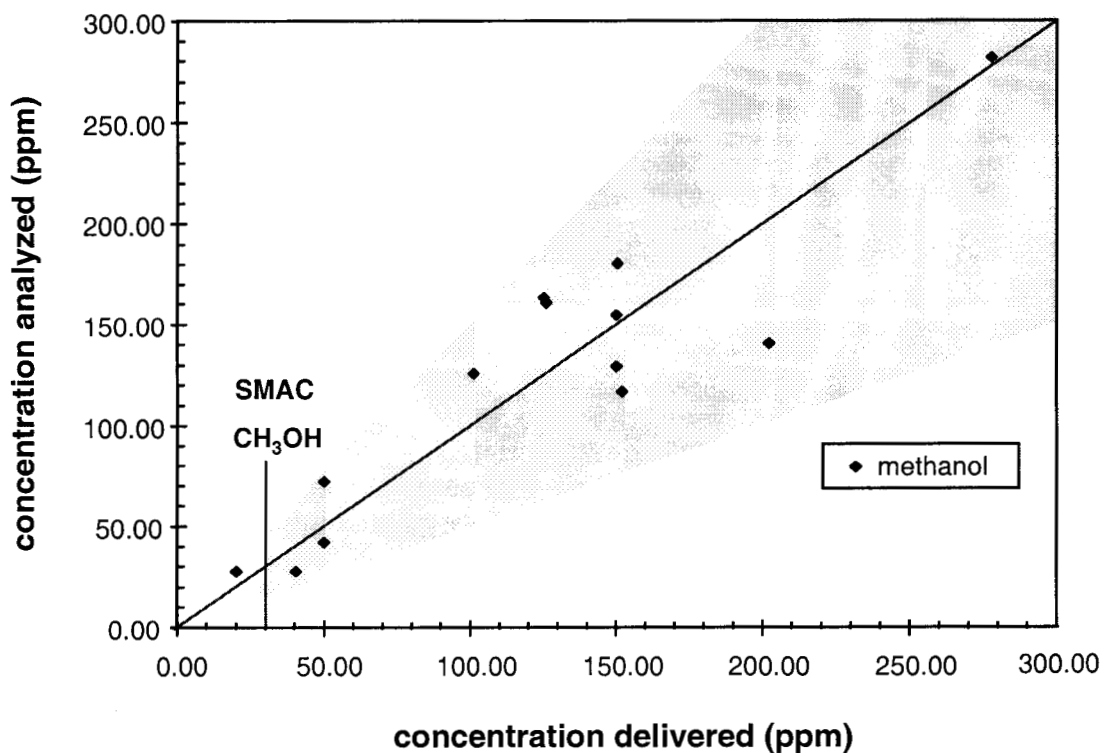
Figure 4d: Identification and Quantification of Methanol. The SMAC is marked on the plot. The shaded area is the +/- 50% target zone.

APPENDIX B: CONFERENCE PROCEEDINGS PAPER

"Monitoring the Air Quality in a Closed Chamber Using an Electronic Nose,"
M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, F. Zee, and J. Graf; presented at
The 27th International Conference on Environmental Systems, Lake Tahoe NV, July
14-17, 1997.

Monitoring the Air Quality in a Closed Chamber Using an Electronic Nose

M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, F. Zee
Jet Propulsion Laboratory, California Institute of Technology
Pasadena CA 91109

J. Graf
Johnson Space Center, NASA
Houston TX 77058

ABSTRACT

An Electronic Nose is being developed at JPL and Caltech for use in environmental monitoring in the International Space Station.   The Electronic Nose (ENose) is an array of 32 polymer film conductometric sensors; the pattern of response may be deconvoluted to identify contaminants in the environment.   An engineering test model of the ENose was used to monitor the air of the Early Human Test experiment at Johnson Space Center for 49 days. Examination of the data recorded by the ENose shows that major excursions in the resistance recorded in the sensor array may be correlated with events recorded in the Test Logs of the Test Chamber.

INTRODUCTION

The ability to monitor the constituents of the breathing air in a closed chamber in which air is recycled is important to NASA for use in closed environments such as the space shuttle and the space station. At present, air quality is determined after the fact by collecting samples and analyzing them on the ground in laboratory analytical instruments such as a gas chromatograph-mass spectrometer (GC-MS).   The availability of a miniature, portable instrument capable of identifying contaminants in the breathing environment at part-per-million levels would greatly enhance the capability for monitoring the quality of recycled air as well as providing notification of the presence of potentially dangerous substances from spills and leaks. Such an instrument is the Electronic Nose now under development at JPL and Caltech [1,2].

An electronic nose is an array of conductometric chemical sensors which change resistance when exposed to vapors. The sensors are not specific to any one vapor; it is in the use of an array of sensors, each with a different sensing medium, that gases and gas mixtures can be identified by the pattern of response of the array. Electronic Noses have been discussed by several authors,

and may be applied to environmental monitoring and quality control in such wide fields as food processing, and industrial environmental monitoring [3,4]. A baseline of "healthy air" is established, and deviations from that baseline are recorded as changes in resistance of the sensors.   The pattern of distributed response of the sensors may be deconvoluted, and contaminants identified and quantified by using a software analysis program such as pattern recognition and/or neural network.

The overall goal of the program at JPL/Caltech is the development of a miniature sensor which may be used to monitor the breathing air in the International Space Station, and which may be coordinated with the environmental control system to solve air quality problems without crew intervention.   Progress to that goal will depend on the success of this portion of the Electronic Nose program, which is the development of a prototype system which will be the subject of an experimental test during a space shuttle flight in 1998.

The Electronic Nose (ENose) now under development at JPL and Caltech is designed to monitor for common contaminants in space shuttle air.   The ENose is not intended to be an analytical instrument such as a GC-MS, although it is being developed with the capacity to identify a limited number of contaminants and metabolic products and to quantify them within 10-20% of their concentration. The goal of this portion of the program is to develop the ability to detect the 12 target compounds listed in Table 1 at levels approximately 1/2 the SMAC (Spacecraft Maximum Allowable Concentration) levels. For most compounds, SMACs are in the single to tens of parts-per-million (ppm) regime. Success of the ENose to detect and quantify contaminants will be confirmed by traditional analyses of air samples with GC-MS.

In the experiment described in this paper, an early developmental model of the ENose was attached to the air recycling line of the Early Human Test Experiment at NASA-Johnson Space Center in January

Compound	Detected on shuttle (ppm) [5]	SMAC (ppm) 1hr / 7day [6,7]
alcohols		
methanol	< 1	30 / 7
ethanol	.5 - 5	---
2-propanol	.4 - 4	400 / 60
methane	1 - 10	5300 /5300
ammonia	0	30 / 0
benzene	< .1	10 / 0.5
CO_2	320	13000 /700
formaldehyde	0	.4/ 0.4
Freon 113	.1 - 1	50 / 50
hydrazine	0	4 / .04
indole	0	1 / .05
toluene	.4 - 4	16 / 16

Table 1: Target compounds for electronic nose shuttle experiment

1997. This experiment offered an early opportunity to determine some of the operating parameters of the ENose and to observe its operation in a closed environment similar to that of the space shuttle or space station. The version of the ENose used in this experiment was an early developmental model, and the analytical software for identification and quantification of contaminants is not yet completed; thus, only qualitative interpretations of events can be made.

EXPERIMENTAL

The Electronic Nose Engineering Development Model: JSC Experiment

An engineering development model of an electronic nose was fabricated at JPL and plumbed in to the air revitalization line of the Early Human Testing Chamber (EHT) at NASA-Johnson Space Center for 49 days in early 1997. Air which was to be recycled in the EHT Air Revitalization System (ARS) was heated to 30 - 34 °C before being passed through the electronic nose chamber. After leaving the ENose chamber, the air was directed to the ARS. The air which passed through the ENose chamber bypassed the EHT testing equipment, then rejoined the air stream to be revitalized.

Presence of a contaminant in air is measured as a change in resistance in the polymer films. Sensor response is expressed as a ratio of resistance at time t=t to resistance at time t=0 (deltaR/R). The electronic circuit for data acquisition has been previously described in detail[9]. Data were acquired on a personal computer using a program written for this purpose in LabView.

Design of Sensor Head   The sensor head of the Electronic Nose used in this experiment consisted of 32 sensor positions arranged on 4 substrates, each with 8 sensor positions. The substrates

were made using hybrid microelectronic cofired ceramic (alumina) processes. Electrodes and contacts were deposited as thick films using screen printing. The substrate layout and fabrication has been discussed in detail elsewhere [8].

In the EHT model, 24 polymeric sensors were made by depositing a solution of polymer mixed with carbon black to make a film 1 - 5 microns thick in contact with gold electrodes. 12 polymers were used in this experiment, four on each of three chips. Each polymer was deposited in 2 positions on each chip. The fourth chip position was occupied by resistors included in the ENose sensor head for electronic reference. A thermistor was included on the sensor head for temperature monitoring. The 12 polymers used are:

A poly(4-vinylphenol)
B poly(styrene-co-allyl alcohol)
C poly(vinylchloride-co-vinyl acetate)
E poly(vinyl acetate)
H poly(styrene)
I poly(styrene-co-maleic anhydride)
J poly(sulfone)
K poly(methyl methacrylate)
M poly(vinyl butyral)
P poly(ethylene-co-vinyl acetate)
Q poly(ethylene oxide)

Deposition of Films   160 mg of each polymer was dissolved in 15 mL of organic solvent. Solvents include tetrahydrofuran (THF), acetone, methylene chloride, toluene or a mixture of solvents. 40 mg of carbon black was added to the solution, and dispersed by sonication. 1 - 3 µL of solution was pipetted onto the sensor area and allowed to dry in air. The resistance of the resulting films was in the range 1 -100 kΩ. Solution was added in increments of 1 µL until the desired

resistance was reached. The use of polymer films as sensing media in an electronic nose has been discussed in detail by several authors, including the Caltech group working with JPL on this project [1-4].

ENose System The ENose developmental system used in this experiment is shown in the diagram in Figure 1.
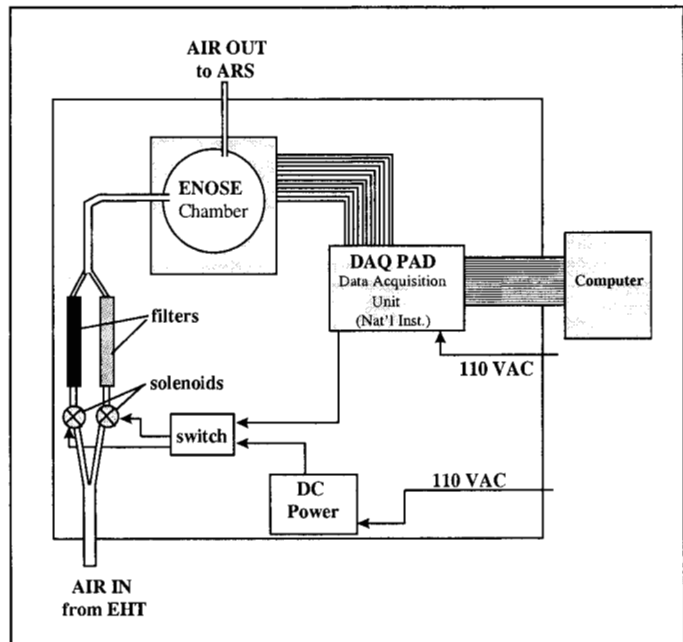
Figure 1: Diagram of ENose system used in EHT experiment

Flowing air (.25 L/min) was taken from the slipstream exiting the EHT chamber, and directed into the ENose system. The air, which had been heated to 30 - 34 °C for EHT testing purposes, was directed either through an activated charcoal filter, put in line to provide clean air baseline data, or though a dummy glass filter, put in line to provide a pressure drop similar to the charcoal filter. Solenoid valves were programmed to open the valve to the charcoal filter and provide 30 minutes of clean air flow every four hours; otherwise, the air went through the glass filter. Air then entered the glass enclosed sensor head chamber where resistance was measured every 30 seconds, and then left the ENose system to enter the air revitalization system of the EHT.

The experiment was controlled using a personal computer and a National Instruments DAQPad. The DAQPad sent commands to the solenoids to open and close, and acquired resistance data from the sensors by measuring the voltage at a current provided by the DAQPad.

A sketch of the sensor chip is shown in Figure 2. Each chip consists of eight sensors approximately 1.5 mm x 2 mm. Polymer films were deposited on the sensor positions as described above.
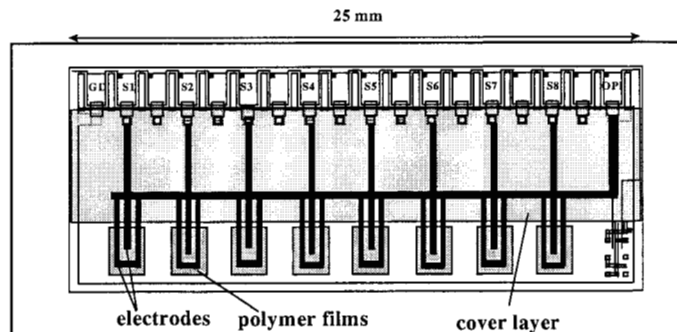
Figure 2: Sketch of the ceramic substrate chip containing eight sensors

Data Analysis The goal of the ENose development is construction of an air quality monitor capable of identifying the target compounds in Table 1 at less than SMAC levels. To accomplish this goal, data analysis software which recognizes the patterns of response of the target compounds is being developed. This software has not been completed, so the data from the EHT experiment may be used only qualitatively.
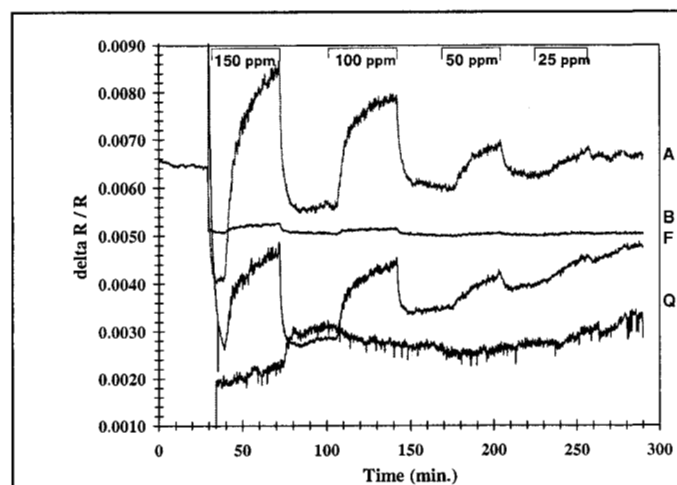
Figure 3: Partial training set for ENose analysis software development. Methanol response of 4 polymers.

ENose data analysis development requires recording training sets of polymer response at the concentrations desired. A sample of a partial training set is shown in Figure 3, where response of 4 polymers to 150, 100, 50 and 25 ppm methanol in air is plotted against time. As may be seen in this figure, different polymers have different magnitudes of response to methanol; polymer Q responds very weakly whereas polymer A has a very strong response. It is these differences which allows identification of compounds; each compound has a unique pattern of response, and magnitude of response may be correlated to concentration of compound. The response to a mixture of compounds has been shown in most cases to be the linear combination of the response to the individual compounds [10].

ENOSE RESPONSE IN EHT

Responses of the ENose have been correlated to several events recorded in the test logs of the EHT. Two of the most notable correlations are shown in Figures 4 and 5.

In Figure 4, spiking in CO_2 levels, as determined by CO_2 measurements made by on line monitoring of the air to be recycled, correlates in time with spikes in ENose sensor response. The magnitude of response for different polymers was different; as shown in the figure, Polymer E responds strongly and Polymer C rather weakly to the changes.

CO_2 concentration fluctuated between .46% and .60% as a percent of chamber air (measured by GC); this is reflected as a fluctuation of a similar magnitude in the most responsive polymer (E). On those days in which CO_2 spiking is not found in the EHT measurements, spiking is not found in the ENose data.

Figure 5 shows significant change in sensor resistance when the EHT chamber door was opened to the outside and untreated air was allowed to enter the chamber. The event in Figure 4 which begins about 8:00 may be correlated to the JSC Test Director Log entry at 8:03 AM (3/14/97).

Transfer in of Dr. Z and a blood draw technician through outerlock door. Mylar screen implemented to secure air integrity.

Subsequent rises in sensor resistance correlate with opening the EHT chamber, and a fall in response correlates with closing the EHT chamber. In spite of the use of a Mylar screen, there was substantial change in constituents in chamber air at the time the outerlock door was opened. There is no independent analysis of the air constituents at that time, so it is possible only to observe the change and correlate it with events recorded in the logs. As the identification software is not yet complete, the sensor responses to opening the chamber cannot be deconvoluted to identify the mixture of compounds inducing the response.

Several other events recorded in the logs or the on line monitoring of the EHT were correlated with response in the ENose, such as change in humidity, water spills and crew report of an odor in the shower area.

CONCLUSIONS

Operation of the ENose for 49 days in the JSC EHT experiment air stream showed that the polymer sensors will respond to events in the breathing air environment. The observation of ENose sensor spiking in temporal correlation with GC observed CO_2 spiking is especially encouraging for use of the ENose in environmental monitoring. The magnitude of CO_2 rise was not sufficient to be a danger to crew members, but the ENose was able to observe the rise, and thus could be used to monitor and quantify the CO_2 levels in an enclosed space.

As may be seen in both Figures 4 and 5, there is little baseline drift over the period of 12 hours. As the sensor is zeroed on clean air provided by the carbon filter, moderate baseline drift, defined as a change over time in the resistance of the polymer in the presence of the same atmosphere, will not affect the operation of the device. However, comparison of the responses of the polymers to cleaned air show that the carbon filter was not sufficiently large to give good cleaning for 49 days. The limit of the filter used is about 15 days of continuous operation. Future investigations will include filter materials capable of longer term operation.

Careful study of the data curves in Figure 4 show a cycling which corresponds to the carbon filter on-off cycle. Temperature measurements showed that turning on the valve to direct air through the carbon filter heated the air by 1-2 $^\circ$C. Many of the polymers are strongly responsive to temperature changes of 1-2 $^\circ$C. Future work also focus on calibration of the temperature response as data which must be included in the data analysis software and on design of a system which is not highly responsive to temperature changes in the environment.

Figure 5, which shows the response of the sensor to outer door activity, shows that the ENose will respond to leaks in a chamber. Further development of the data analysis software and the low concentration monitoring capacity of the device will lead to a miniature instrument for environmental monitoring and early detection and identification of changes in environmental constituents.

Development of the low concentration monitoring capacity of the ENose will be accomplished by improving the polymer response and by diminishing the noise in the electronics response. Polymer response improvement includes development of application methods and determination of optimum carbon loading and film thickness.
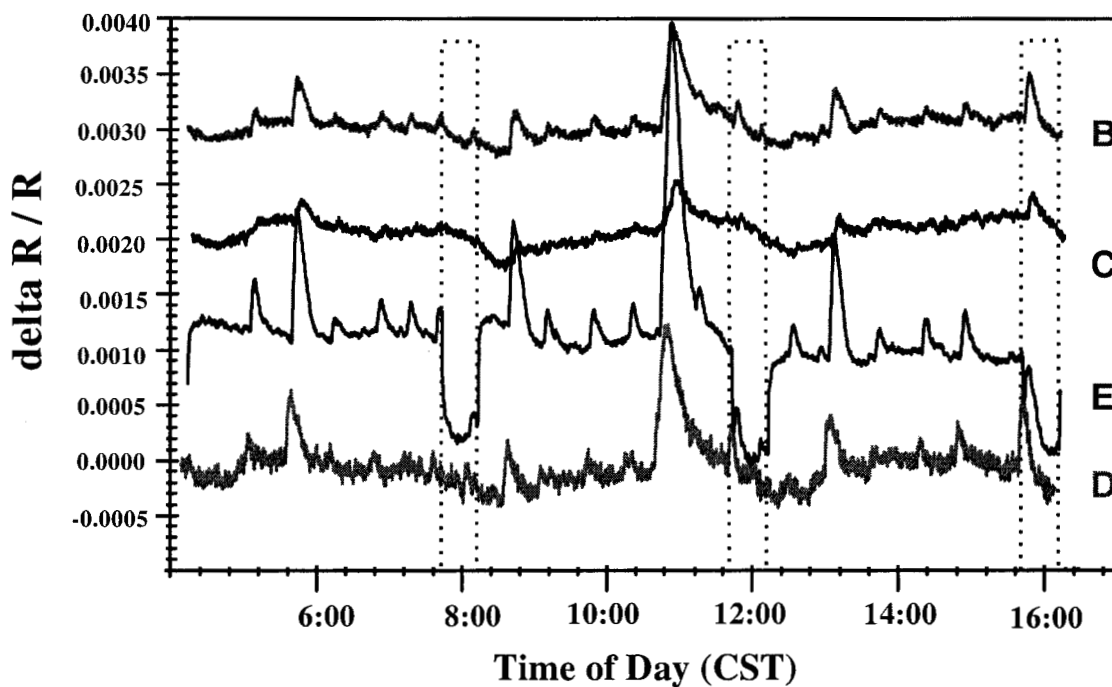
Figure 4: Spiking in EHT air CO_2 levels may be correlated to spikes in Enose sensor response at the same time. Dotted vertical lines show the 30 minute reference cycle with a corresponding dip in sensor response.
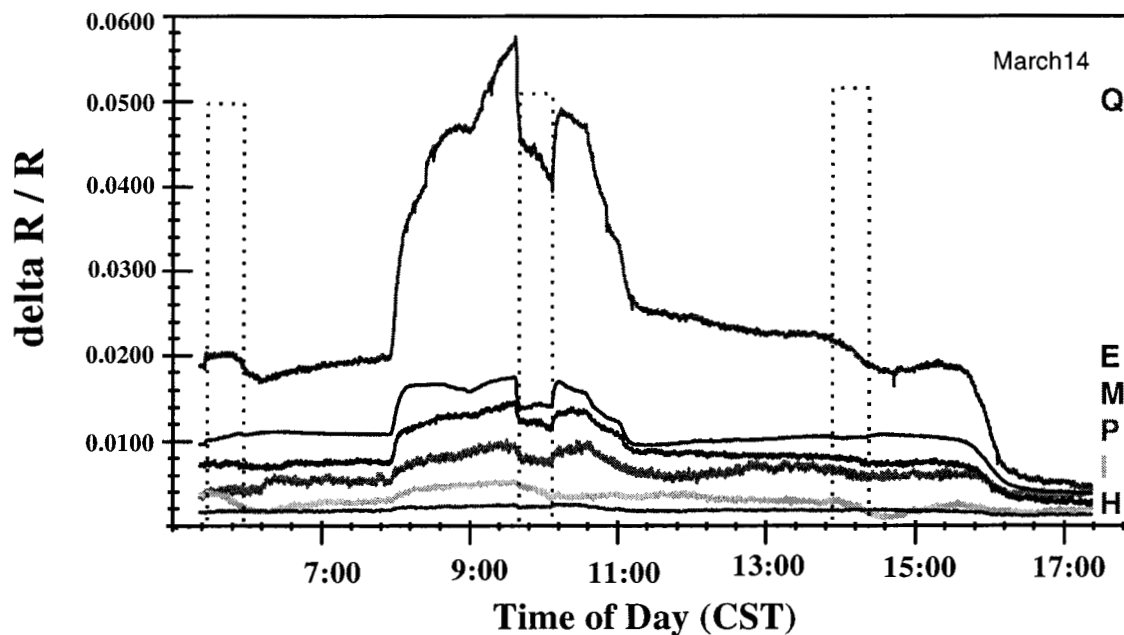
Figure 5: When the EHT chamber door was opened, there is significant change in resistance in Enose sensors. Dotted vertical lines show 30 minute reference cycles with a corresponding dip in sensor response.

The goal of this portion of the ENose development program is demonstration of the ability of the device to recognize and quantify the 12 contaminants listed in Table 1. It is intended that a demonstration experiment be performed with the ENose on a Shuttle flight in 1998. Demonstration of the ENose's ability to detect leaks and unusual events in the JSC EHT experiment shows that with development of analysis software, it will be possible to build a miniature environmental monitoring device.

ACKNOWLEDGMENTS

REFERENCES

1. M.S. Freund and N.S. Lewis, *Proc. National Academy of Science*, **92**, 2652, (1995).
2. M.C. Lonergan, E.J. Severin, B.J. Doleman, S.A. Beaber, R.H. Grubbs and N.S. Lewis, *Chem. Materials,* **8**, 2298 (1996).
3. H.V. Shurmer and J.W. Gardner, *Sensors and Actuators*, **B8**, 8, (1992).
4. J.W. Gardner, T.C. Pearce, S. Friel, P.N. Bartlett and N. Blair, *Sensors and Actuators*, **B18-19**, 240, (1994).
5. J.T. James, *et al.*, *Aviation, Space Environ. Med.*, **65**, 851 (1994).
6. *Spacecraft Maximum Allowable Concentrations for Selected Airborne Contaminants*, Vols. 1 & 2, National Academy Press, Washington, DC (1994).
7. *Space Physiology and Medicine*, A.E. Nicagossian, C.L. Hunton & S.L. Pool, eds., Lea and Febiger, Philadelphia (1994).
8. M.G. Buehler and M.A. Ryan, *Proc. Int'l Conf. on Microelectronic Test Structures* (March 1996).
9. M.G. Buehler and M.A. Ryan. *Proc. SPIE Conf. on Electro-Optical Tech. for Chemical Detection*, (April, 1997).
10. N.S. Lewis. California Institute of Technology, private communication.

APPENDIX C: CREW PROCEDURES FOR FLIGHT EXPERIMENT

ENOSE ACTIVATION

1. Remove ENose from locker
2. Remove and discard protective paper from hook and pile fasteners. Attach ENose to locker TBD
3. Connect prerouted ENose power cable P/N 10108-10082-06 to ENose PWR connector
4. Check that ENose PWR - OFF
5. Connect ENose power cable to PPDB J2 connector

<u>NOTE</u>
Immediately following ENose PWR ON, PWR MEASURE LED will illuminate (green).
After approx. 60 secs internal solenoid will cycle (audible click) and
BASELINE LED will briefly illuminate (green), then off.
Low audible beep, then 10 secs later audible fanfare.
Internal pump then turns on and remains on (audible buzzing sound).
Within 15 - 20 sec after power on, green PWR MEASURE LED
blinks amber approximately every 15 sec

6. ENose PWR - ON
   Log PWR ON MET: _____/_____:_____
7. √ PWR MEASURE LED - illuminated (green)
8. √ Air flow or buzz of internal pump audible

```
*          If PWR MEASURE LED is not illuminated green            *
*          and/or no airflow or buzz of internal pump not audible,  *
*          perform 1.4a, ENOSE PWR MEASURE                         *
*          LED NOT ILLUMINATED                                     *
*                                                                  *
*          If PWR MEASURE LED is not blinking amber                *
*          ENose PWR - OFF, wait 10 sec                            *
*          ENose PWR - ON                                          *
*          Log PWR ON MET: _____/_____:_____                       *
*          Wait 20 sec                                             *
*          Report to MCC, status of PWR MEASURE LED and            *
*              PWR ON MET                                          *
```

9. Take two photos documenting deployed setup
10. Report PWR ON MET to MCC

ENOSE DAILY MARKER

<u>NOTE</u>
Mark 1 must be performed at least 2 hrs after initial ENose activation
and be complete by 3 hrs after activation, or
be performed in next available 3-hr period.
No wait is required after any subsequent restart.

1. Remove alcohol wipe kit and one Grab Sample Container (GSC)
2. Temp stow alcohol wipe kit
3. Complete E-Nose Daily Marker Data sheet block 1.
If illuminated, wait to perform alcohol wipe operation (step 8) until green BASELINE LED is off (approx 15 min)
4. Complete ENose Daily Marker Data Sheet blocks 2-3
5. Using procedure on GSC, collect air sample at 10 to 25 cm in front of ENose air inlet
6. Temp stow GSC
7. Complete ENose Daily Marker Data Sheet block 4
8. Remove one alcohol wipe and gently wave it at 5 to 10 cm in front of the ENose air inlet for 30 to 60 sec
9. Replace alcohol wipe in its wrapper
10. Discard alcohol wipe/wrapper away from ENose
11. Complete ENose Daily Marker Data Sheet block 5.
12. For continuous 20 sec,

√ green PWR MEASURE LED - blinking amber approx. every 15 sec

* If PWR MEASURE LED is not blinking amber	*
* ENose PWR - OFF, wait 10 sec	*
* ENose PWR - ON	*
* Log PWR ON MET: ____/_____:_____	*
* Wait 20 sec	*
* Report to MCC, status of PWR MEASURE LED and	*
* PWR ON MET	*

13. Complete ENose Daily Marker Data Sheet block 6
14. Restow GSC, alcohol wipe kit
15. Complete ENose Daily Marker Data Sheet blocks 7 and 8.
16. Call MCC, report illumination status of green BASELINE LED, GSC completion MET

ENOSE RESTART

1. ENose PWR - OFF, wait 10 sec
2. ENose PWR - ON, log PWR ON MET: _____/_____:_____
3. √ PWR MEASURE LED - illuminated (green)
4. √ air flow or buzz of internal pump audible

> *   If PWR MEASURE LED is not illuminated green   *
> *   and/or no air flow or buzz of internal pump not audible, *
> *   perform 1.4a, ENOSE PWR MEASURE LED   *
> *   NOT ILLUMINATED   *

5. Report PWR ON MET to MCC

ENOSE DEACTIVATION

1. ENose PWR - OFF
2. Log MET: _____/_____:_____
3. Disconnect ENose power cable from ENose box and PPDB, secure cable ends
4. Stow ENose

APPENDIX D: ENose STS95 flight data analysis result, LMNLS method

Lines which contain identification and quantification of the daily markers (wipe events) are in blue type.

1 ben	2 eth	3 fre	4 ind	5 CH4	6 MeOH	7 pro	8 tol	9 amm	10 for	11 wat	12 deltaRH	13 wipe	GMTtime mmddhrmn	filetime	%rsdu
0	0	0	0	0	0	0	0	0	0	0	13	332	10310004	102910130	7
0	0	0	0	0	0	0	0	0	0	0	19	0	10310025	102910151	7
0	0	0	0	0	0	0	0	0	0	0	12	0	10310238	102910284	7
0	0	0	0	0	0	0	0	0	0	0	8	0	10311319	102920135	3
0	0	0	0	0	0	0	0	0	0	0	9	0	10311633	102920329	5
0	0	0	0	0	0	0	0	0	0	0	8	0	10312147	102920643	6
0	0	0	0	0	0	0	0	0	0	0	0	402	10312232	102920688	6
0	0	0	0	0	0	0	0	0	0	0	10	0	11010128	102930076	5
0	0	0	0	0	0	0	0	0	0	0	9	0	11010155	102930103	4
0	0	0	0	0	0	0	0	0	0	0	7	0	11010252	102930160	7

1	2	3	4	5	6	7	8	9	10	11	12	13			
0	0	0	0	0	0	0	0	0	0	0	6	0	11010601	102930349	4
0	0	0	0	0	0	0	0	0	0	0	8	0	11011409	102940050	5
0	0	0	0	0	0	0	0	0	0	0	9	0	11011601	102940161	5
0	0	0	0	0	0	0	0	0	0	0	7	0	11011814	102940295	5
0	0	0	0	0	0	0	0	0	0	0	9	0	11011855	102940336	4
0	0	0	0	0	0	0	0	0	0	0	7	330	11012333	102940613	4
0	0	0	0	0	0	0	0	0	0	0	10	0	11020104	102940704	5
0	0	0	0	0	0	0	0	0	0	0	9	0	11020636	102950249	5
0	0	0	0	0	0	0	0	0	0	0	5	0	11021039	102950493	6
0	0	0	0	0	0	0	0	0	0	0	10	0	11021447	102950740	7

1	2	3	4	5	6	7	8	9	10	11	12	13			
0	0	0	0	0	0	0	0	0	0	0	10	0	11021739	102960124	6
0	0	0	0	0	0	0	0	0	0	0	11	0	11021911	102960216	5
0	0	0	0	0	0	0	0	0	0	0	0	910	11022148	102960374	6
0	0	0	0	0	0	0	0	0	0	0	8	0	11022302	102960448	5
0	0	0	0	0	0	0	0	0	0	0	10	0	11022323	102960469	8
0	0	0	0	0	0	0	0	0	0	0	14	0	11030028	102960534	5
0	0	0	0	0	0	0	0	0	0	0	7	0	11030712	102970150	4
0	0	0	0	0	0	0	0	0	0	0	7	0	11031524	102970643	6
0	0	0	0	0	0	0	0	0	0	0	7	0	11031651	102970729	7
0	0	0	0	0	0	0	0	0	0	0	5	0	11031703	102970741	7

1	2	3	4	5	6	7	8	9	10	11	12	13			
0	0	0	0	0	0	0	0	0	0	0	9	0	11031846	102980058	5
0	0	0	0	0	0	0	0	0	0	0	9	0	11031932	102980103	6
0	0	0	0	0	0	0	0	0	0	0	8	296	11032213	102980264	4
0	0	0	0	0	0	0	0	0	0	0	12	0	11032230	102980282	5
0	0	0	0	0	0	0	0	0	0	0	10	0	11032303	102980315	4
0	0	0	0	0	0	0	0	0	0	0	7	63	11032324	102980336	5
0	0	0	0	0	0	0	0	0	0	0	10	0	11041152	102990298	4
0	0	0	0	0	0	0	0	0	0	0	10	0	11041424	102990449	6
0	0	0	0	0	0	0	0	0	0	0	9	0	11041740	102990645	6
0	0	0	0	0	0	0	0	0	0	0	8	513	11042128	103000087	5

1	2	3	4	5	6	7	8	9	10	11	12	13			
0	0	0	0	0	0	0	0	0	0	0	6	0	11042144	103000103	7
0	0	0	0	0	0	0	0	0	0	0	7	0	11042232	103000151	5
0	0	0	0	0	0	0	0	0	0	0	6	0	11042350	103000228	6
0	0	0	0	0	0	0	0	0	0	0	9	0	11050146	103000345	5
0	0	0	0	0	0	0	0	0	0	0	7	0	11050414	103000493	5
0	0	0	0	0	0	0	0	0	0	0	9	0	11052041	103010692	9

APPENDIX E: REPORT ON ANALYSIS OF GRAB SAMPLE CONTAINERS FROM STS-95

wyle
laboratories
Life Sciences, Systems and Services

TO: John T. James, Ph.D./SD2 Technical Monitor

FROM: Thomas F. Limero, Ph.D./Toxicology Laboratory Supervisor

SUBJECT: Results from the Analyses of STS-95 Mission Air Samples
for Supporting the E-Nose Experiment

DATE: January 8, 1999

INTRODUCTION

An environmental monitoring prototype called the E-Nose was supported by the Toxicology Laboratory on STS-95. Toxicology support for this experiment consisted of providing seven instantaneous grab samplers for air sample collected near the operating E-Nose during the mission and the subsequent groundbased analyses of these air samples. This report presents the groundbased analyses of the air contaminants in the grab samples from STS-95 and quality assurance data that verifies the results. The results in this report will be compared to the real time sensor data acquired by the E-Nose during the mission.

The Toxicology Laboratory of the Medical Operations Branch at the Johnson Space Center processed and analyzed seven air samples from STS-95 for the E-Nose experiment. Seven grab sample containers (GSC) were used to collect air samples in the Discovery mid-deck for the period MET day 1 to MET day 7. A backup GSC was not used during the mission and was assigned as a trip control. The samples and the trip control were returned to the Toxicology Laboratory on November 10,1998 for analyses through the United Space Alliance Flight Equipment Processing Center.

GRAB SAMPLE CONTAINERS (GSC)

Sample Log: GSC

Tracking Number	Container Number	Sample Location	Sample Time	Date Received
AA02359	1043	MID-DECK	MET 1\4:40	11/10/98
AA02360	1035	MID-DECK	MET 2\3:10	11/10/98
AA02361	1046	MID-DECK	MET 3\4:05	11/10/98
AA02362	1038	MID-DECK	MET 4\2:22	11/10/98
AA02363	1020	MID-DECK	MET 5\2:48	11/10/98
AA02364	1039	MID-DECK	MET 6\2:05	11/10/98
AA02365	1080	MID-DECK	MET 7\1:57	11/10/98
AA02366	1036	TRIP CONTROL		12/08/98

Analysis: GSC

The GSC air samples and the trip control were analyzed using both GC and GC/MS methods according to the Toxicology Laboratory ISO-9000 Work Instructions (WI-TOX-003) "Measurement of VOCs in Spacecraft Air Using Grab Sample Containers" and (WI-TOX-004) "Gas Chromatography Analysis of Methane, Ethylene, Hydrogen, Carbon Monoxide, and Carbon Dioxide in Spacecraft Air Using Grab Sample Containers." GC and GC/MS analyses were initiated immediately after receipt of the samples.

Results: GSC

The analytical results are reported in Table 1. Quantitation of TO-14/polar compounds, and GC target compounds was derived from calibration curves, while the quantitation of other compounds was based upon response factors available in the literature (see WI-TOX-003 for details). All GC/MS target compounds were identified and quantified if their base peak area was greater than 0.5% of the fluorobenzene base peak area. No attempt was made to identify nontarget compounds with peak areas of less than 20% of the fluorobenzene standard peak area, as these compounds would have little effect on the toxicological assessment of the Orbiter's breathing air quality. However, if a significant non-target compound (i.e. above 20% of fluorobenzene peak area) was detected in one GSC air sample, this compound was searched for in other samples. Compound concentrations listed as "< the laboratory report detection limit" indicate that this target compound was analyzed for, but not detected.

Sulfur hexafluoride (SF6) was detected in all STS-95 air samples, by using the GC/TCD method for hydrogen analyses. The concentrations of SF6 were not calculated because of the low toxicity of the compound and the current unavailability of a standard.

QA/QC: GSC

Each sample container was cleaned, proofed, certified leak-free, and prepared for shipment to Kennedy Space Center in the JSC Toxicology laboratory according to WI-TOX-010 "Cleaning Summa-Treated Canister" specifications. After the containers were evacuated, 10cc of surrogate standard (1480ppb of each component prepared on 4/10/98) was injected into each using a pre-conditioned 20cc syringe on 9/17 /98. Following the dosing procedures, each GSC was individually bagged to "clean room" requirements and delivered to the Flight Equipment Processing Center for bench review and transfer to KSC. Recoveries of surrogate standards from the STS-95 air samples and the trip control are presented in Table 2. All recoveries were within advisory QC limits. Pressure for each GSC air sample was measured and recorded during the sample analysis process. These data are presented in Table 3. All GSC air samples appeared to be leak-free.

Verification of instrument function and adherence to Toxicology Laboratory Work Instructions was documented for GSC air sample analyses by the completed "GC Method Calibration and

Blank Summary" and "Volatile Organic GC/MS Tuning and Mass Calibration-Bromofluorobenzene (BFB)" forms presented in Appendix 1.

Abnormalities: GSC

 None

QA/QC

TABLE 1
ANALYTICAL RESULTS OF
E-NOSE STS-95 GSC AIR SAMPLES

CHEMICAL CONTAMINANT	CONCENTRATION (mg/m3)							
	AA02359 #1043 MET 1\4:40	AA02360 #1035 MET 2\3:10	AA02361 #1046 MET 3\4:05	AA02362 #1038 MET 4\2:22	AA02363 #1020 MET 5\2:48	AA02364 #1039 MET 6\2:05	AA02365 #1080 MET 7\1:57	AA02366 #1036 Trip Ctrl
TARGET COMPOUNDS (TO-14/POLAR)								
DICHLORODIFLUOROMETHANE (F12)	#TRACE	TRACE	TRACE	0.07	0.07	0.06	0.06	<0.050
CHLOROMETHANE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
1,2-DICHLORO-1,1,2,2-TETRAFLUOROETHANE (F114)	*<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
ACETALDEHYDE	0.07	0.07	0.13	0.10	0.10	0.08	0.06	TRACE
METHANOL	0.22	0.25	0.35	0.29	0.27	0.21	0.22	TRACE
VINYL CHLORIDE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
BROMOMETHANE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
ETHANOL	2.7	1.8	3.3	2.1	3.8	1.9	2.4	TRACE
CHLOROETHANE	TRACE	TRACE	TRACE	<0.050	<0.050	<0.050	<0.050	<0.050
PROPENAL	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.020
ACETONE	0.35	0.31	0.55	0.48	0.50	0.40	0.35	TRACE
PROPANAL	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE
ISOPROPANOL	0.51	0.72	4.8	13	7.8	2.1	2.0	TRACE
TRICHLOROFLUOROMETHANE (F11)	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
FURAN	<0.050	TRACE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
ACRYLONITRILE	<0.050	TRACE	TRACE	TRACE	TRACE	<0.050	TRACE	<0.050
2-METHYL-2-PROPANOL	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
METHYL ACETATE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
1,1-DICHLOROETHENE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
DICHLOROMETHANE	0.15	0.18	0.21	0.24	0.24	0.20	0.20	<0.050
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE (F113)	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE
N-PROPANOL	<0.050	<0.050	TRACE	TRACE	TRACE	<0.050	<0.050	<0.050
1,1-DICHLOROETHANE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
BUTANAL	TRACE	<0.050	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE
2-BUTANONE	TRACE	TRACE	0.06	TRACE	TRACE	TRACE	TRACE	TRACE
1,2-DICHLOROETHENE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
2-METHYLFURAN	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
ETHYL ACETATE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
CHLOROFORM	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
2-BUTENAL	<0.050	<0.050	TRACE	TRACE	TRACE	TRACE	<0.050	<0.050
1,2-DICHLOROETHANE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
1,1,1-TRICHLOROETHANE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
N-BUTANOL	0.10	0.11	0.12	0.14	0.12	0.09	0.09	TRACE
1,1-DICHLOROPROPENE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
BENZENE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
CARBON TETRACHLORIDE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
2-PENTANONE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
PENTANAL	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE
1,2-DICHLOROPROPANE	<0.050	<0.050	<0.050	TRACE	<0.050	<0.050	<0.050	<0.050
TRICHLOROETHENE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
2,5-DIMETHYLFURAN	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
CIS-1,3-DICHLOROPROPENE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
2-PENTENAL	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
TRANS-1,3-DICHLOROPROPENE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
1,1,2-TRICHLOROETHANE	<0.050	<0.050	<0.050	<0.050	<0.050	≤0.050	<0.050	<0.050
TOLUENE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
HEXANAL	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE
MESITYL OXIDE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
1,2-DIBROMOETHANE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
BUTYL ACETATE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
TETRACHLOROETHENE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
CHLOROBENZENE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
ETHYL BENZENE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
M- + P-XYLENES	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
2-HEPTANONE	TRACE	<0.050	TRACE	TRACE	TRACE	TRACE	<0.050	<0.050
CYCLOHEXANONE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
HEPTANAL	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE
STYRENE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050
1,1,2,2-TETRACHLOROETHANE	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
O-XYLENE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	<0.050